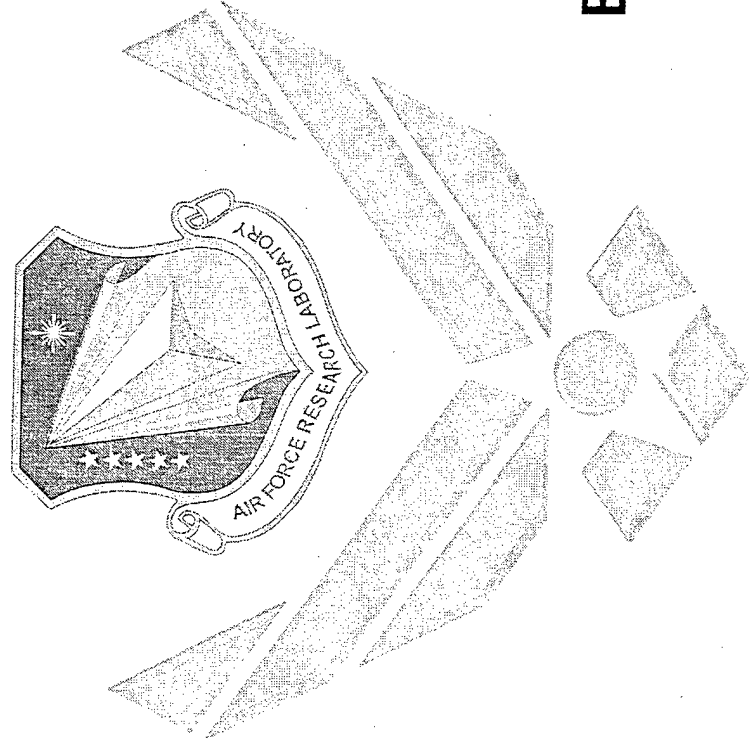


REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
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				5c. PROGRAM ELEMENT NUMBER	
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					19b. TELEPHONE NUMBER (include area code) (661) 275-5865

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Fluorinated Polyhedral Oligomeric Silsesquioxanes (FluoroPOSS)

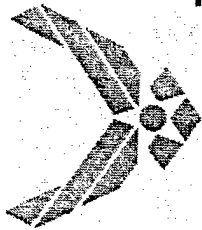


*Silicones and Silicone-
Modified Materials*

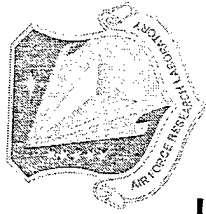
April 1, 2004

JM Mabry, A Vij, D Marchant,
BD Viers, PN Ruth, and CE Schlaefer
Polymer Working Group
Air Force Research Laboratory
(661)275-5857

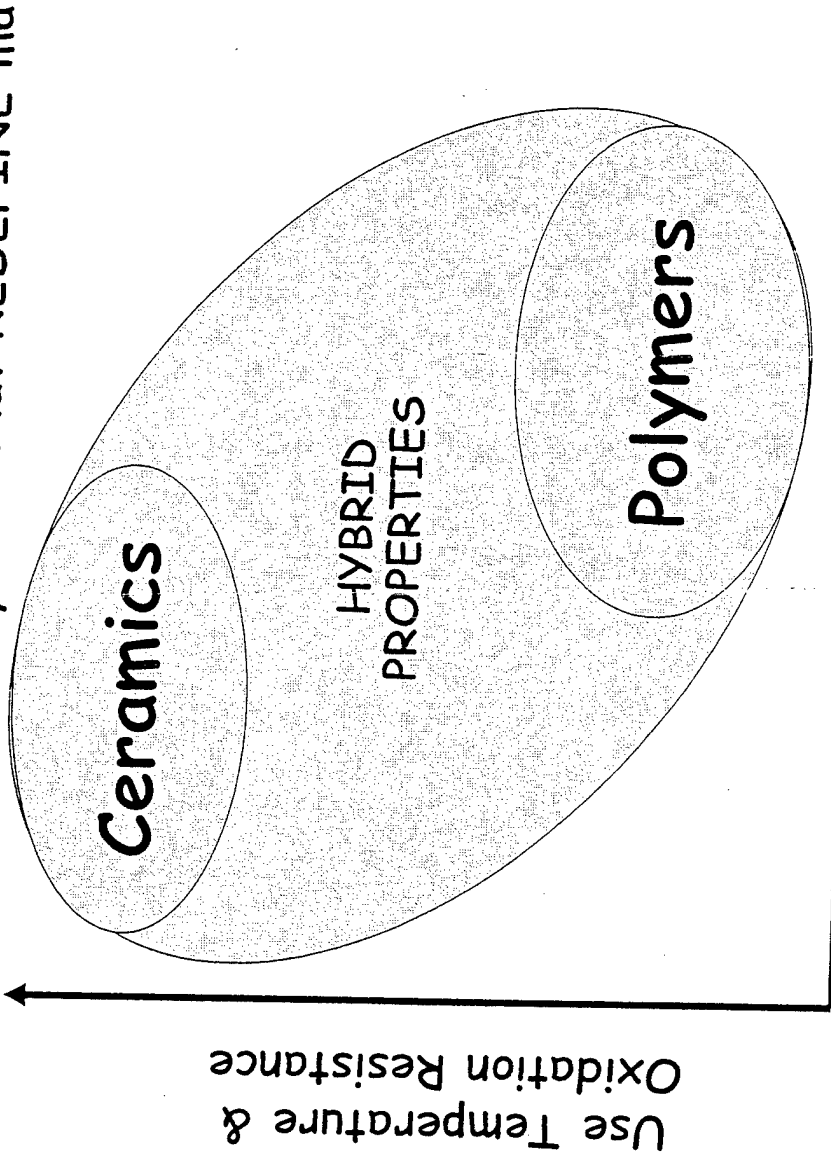
joseph.mabry@edwards.af.mil



Hybrid Inorganic/Organic Polymers



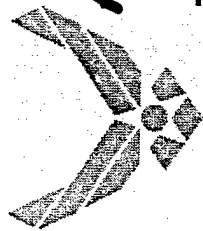
Goal: Develop High Performance Polymers that REDEFINE material properties



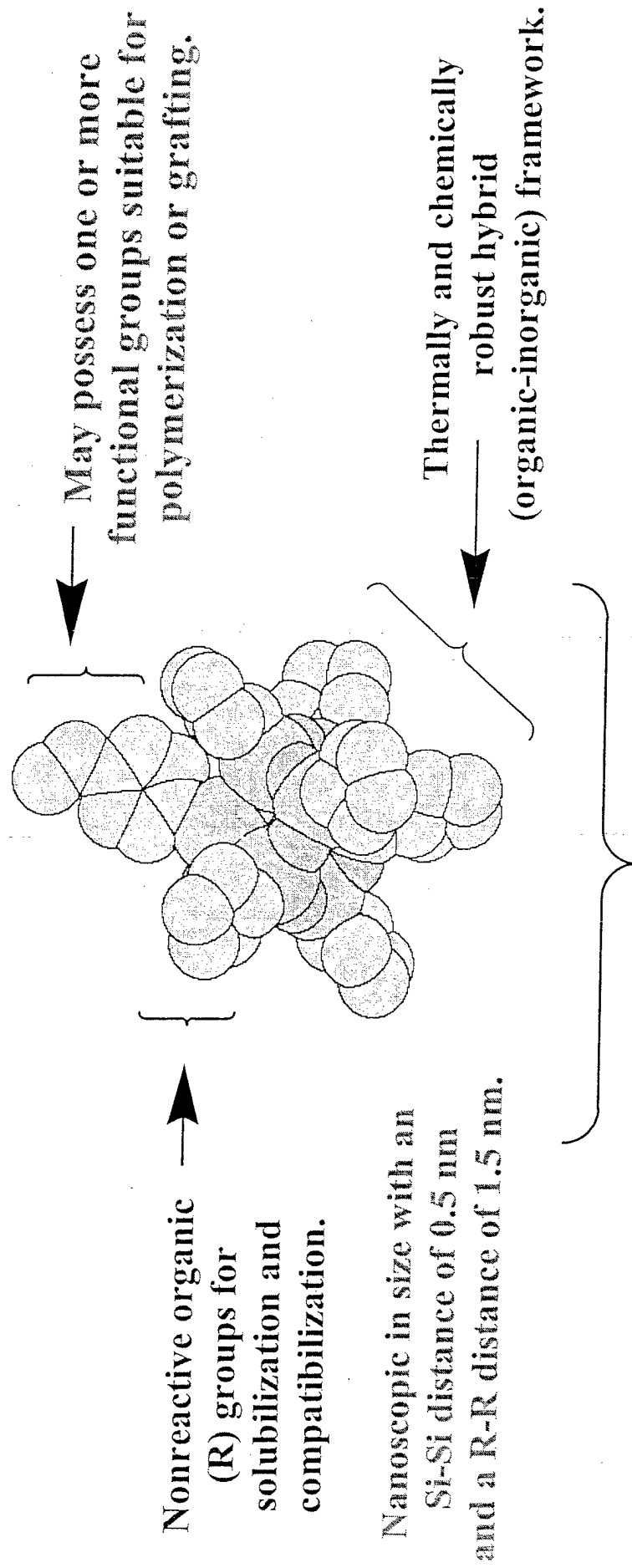
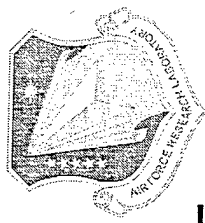
PAS-03-061

• Hybrid plastics bridge the differences between ceramics and polymers

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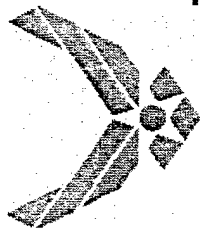
Anatomy of a POSS Nanostructure



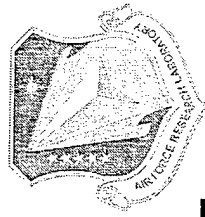
Precise three-dimensional structure for molecular level reinforcement of polymer segments and coils.

PAS-03-061

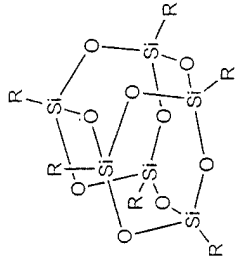
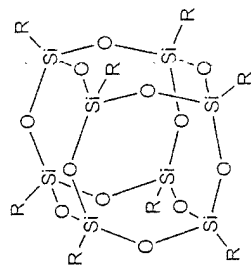
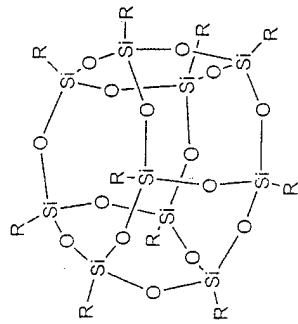
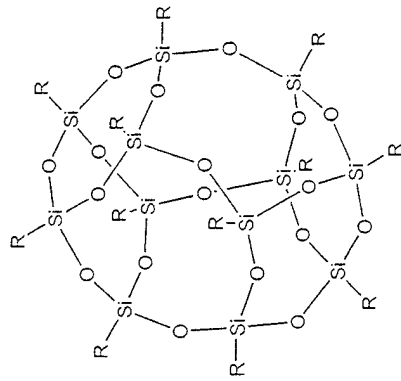
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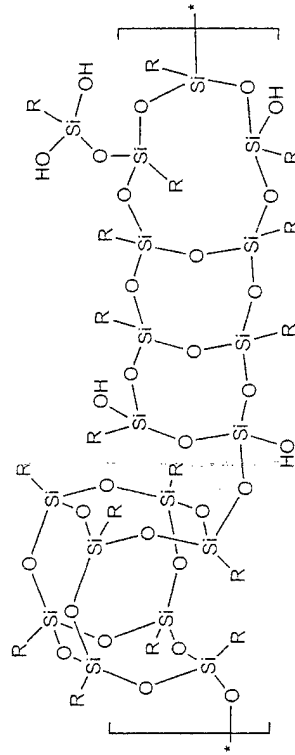
POSS Synthesis



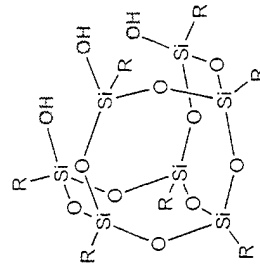
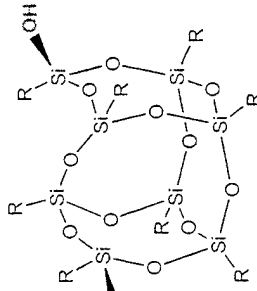
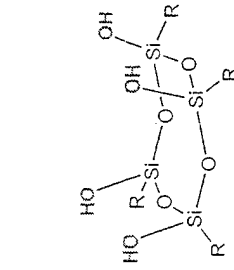
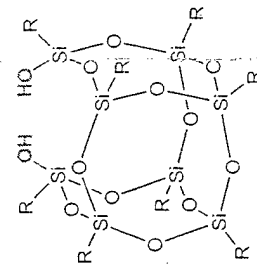
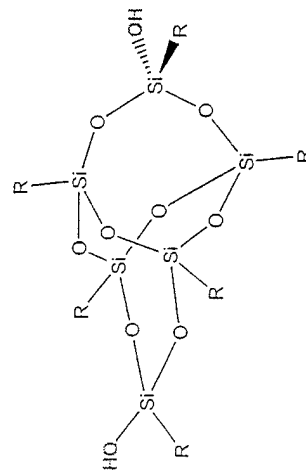
RSiX₃ acid or base hydrolysis



Completely condensed



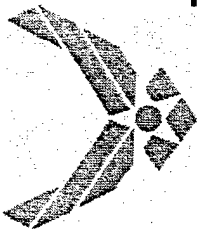
Resin



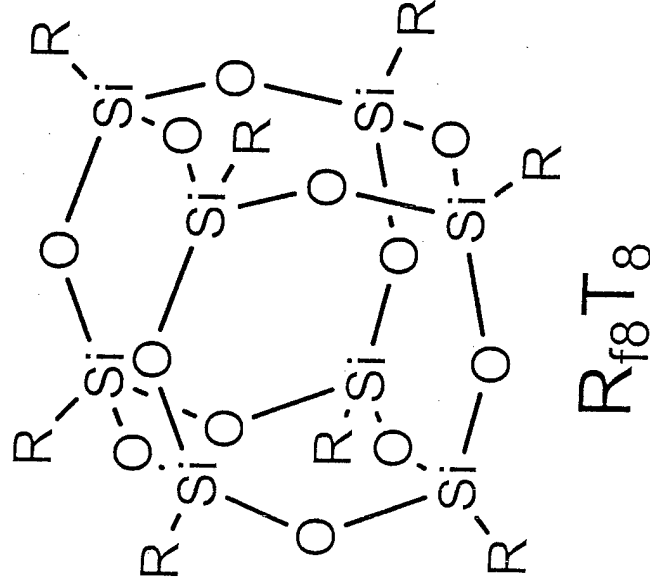
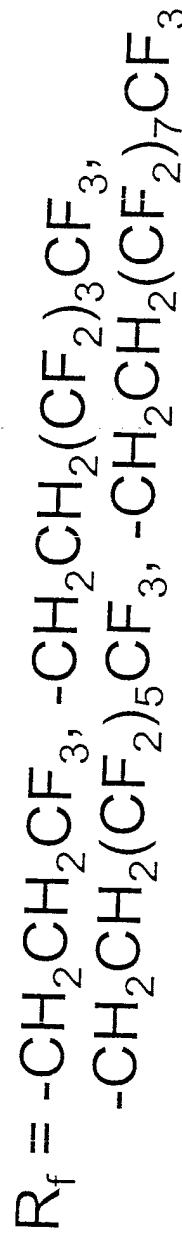
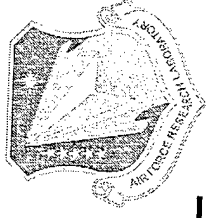
Incompletely condensed

Brown, Feher, AFRL, Hybrid Plastics

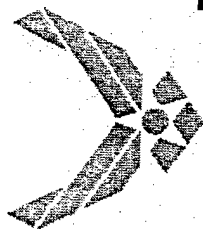
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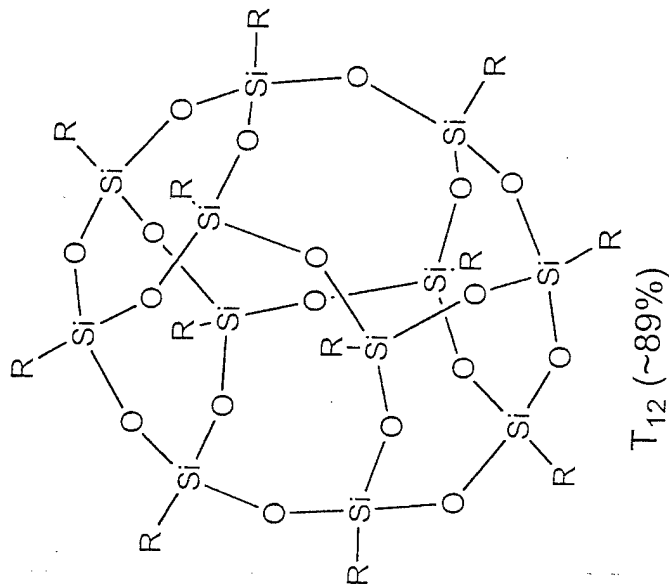
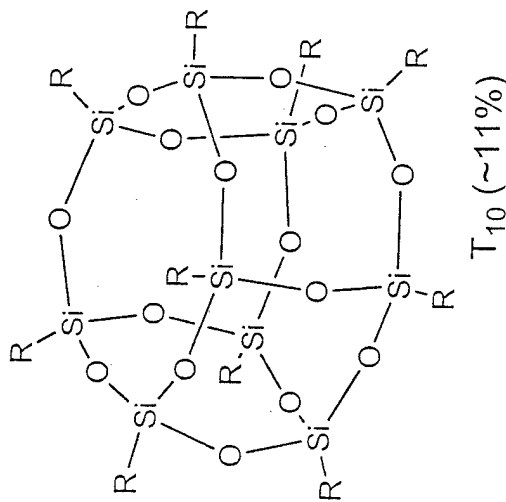
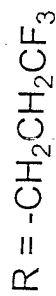
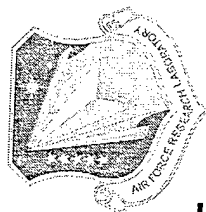
FluoroPOSS Synthesis



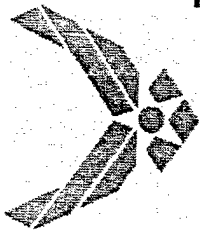
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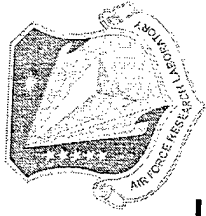
Fluoropropyl T_n



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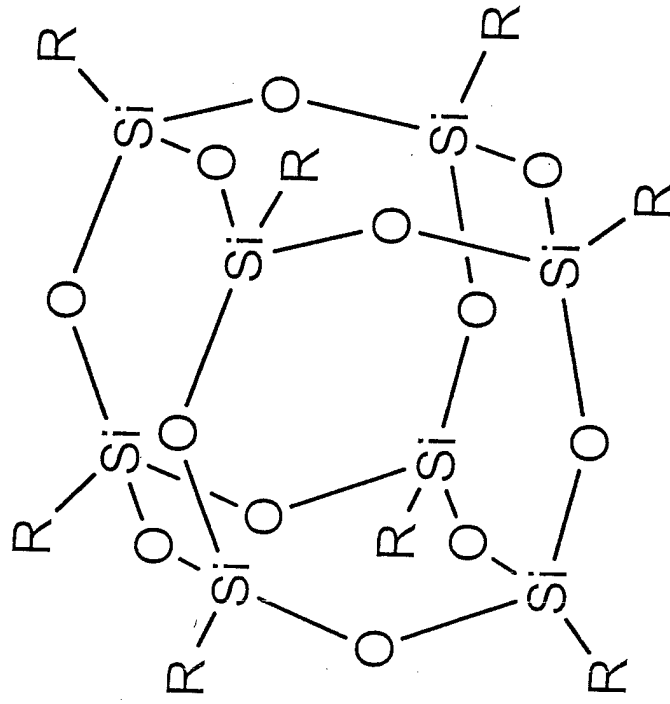


Fluorodecyl₈T₈

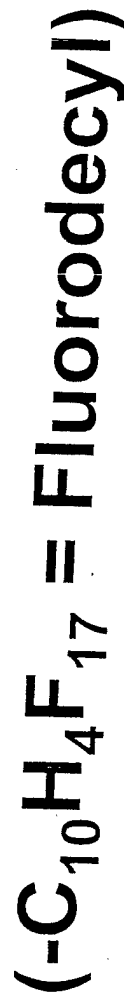


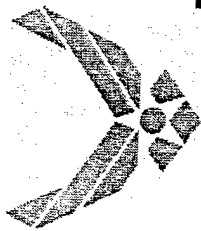
$$M_W = 3993.54 \text{ g/mol}$$

$$\rho = 2.058 \text{ g/mL}$$

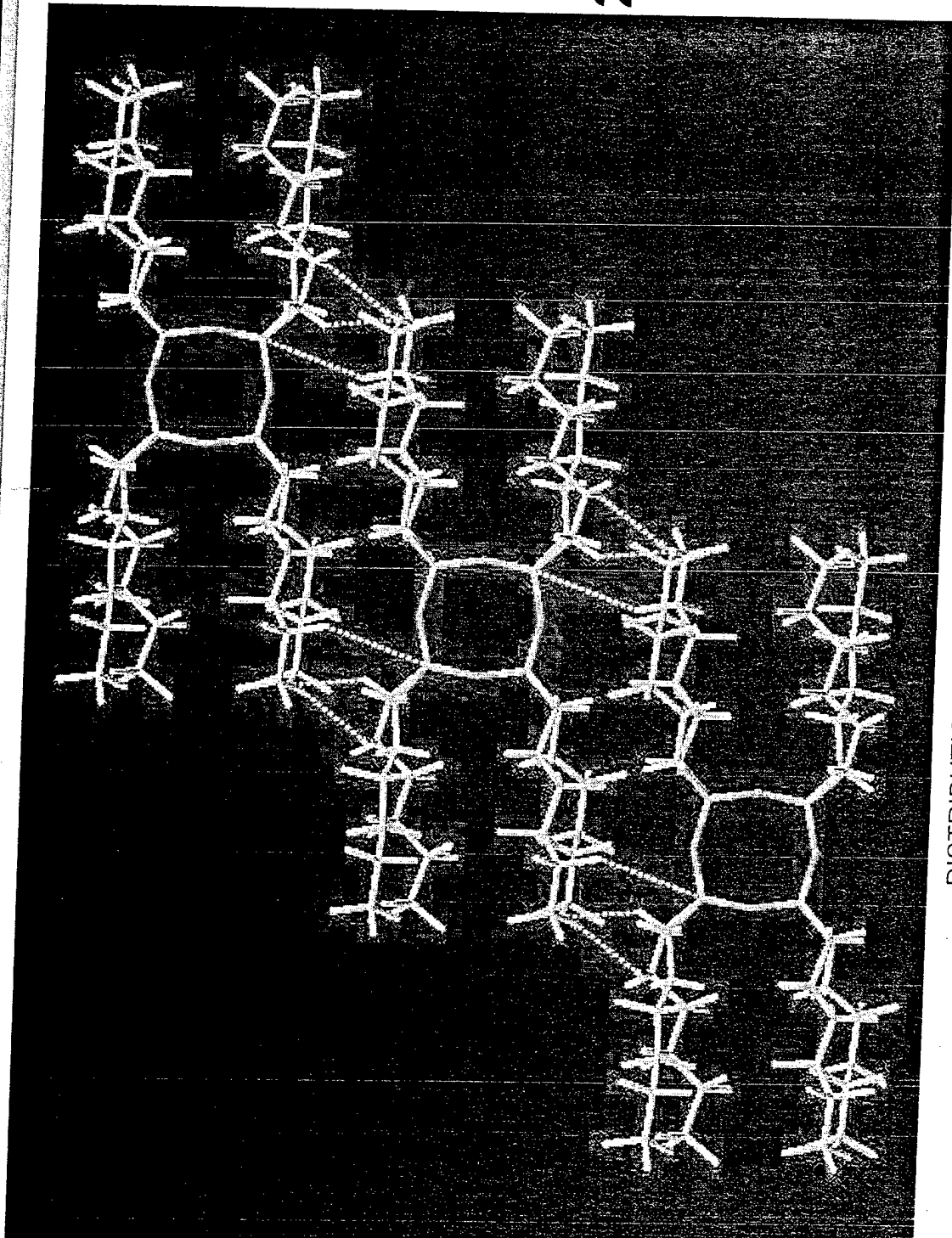
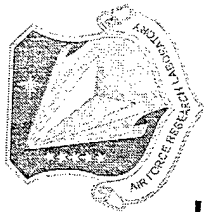


T₈





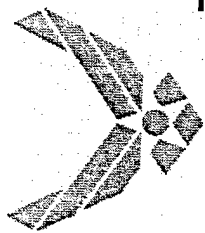
Fluorohexyl₈T₈



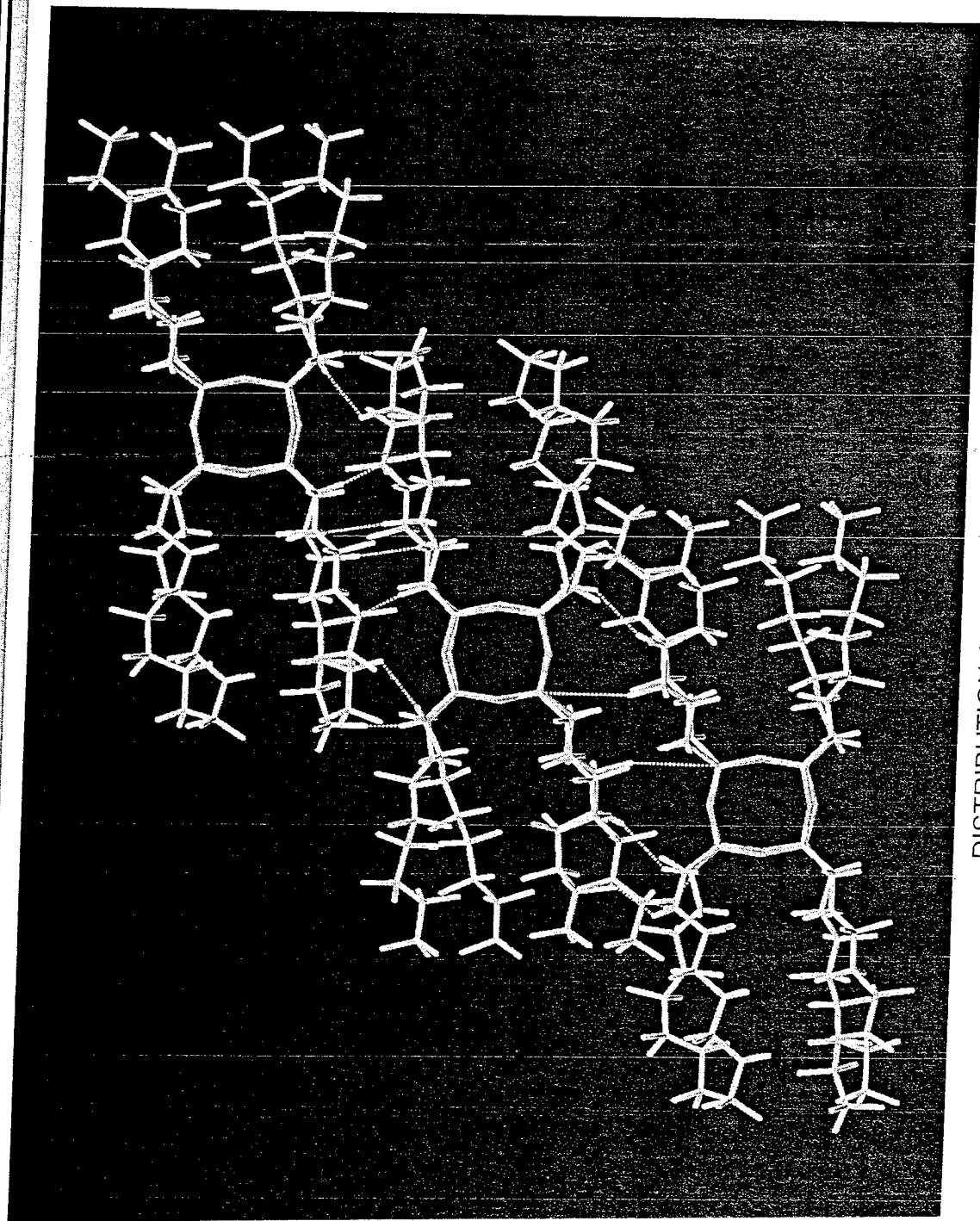
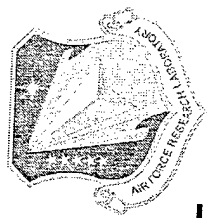
$$\rho = 1.98 \text{ g/mL}$$

$$M_w = 2393.33 \text{ g/mol}$$

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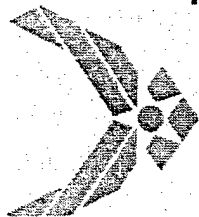
Fluorooctyl₈T₈



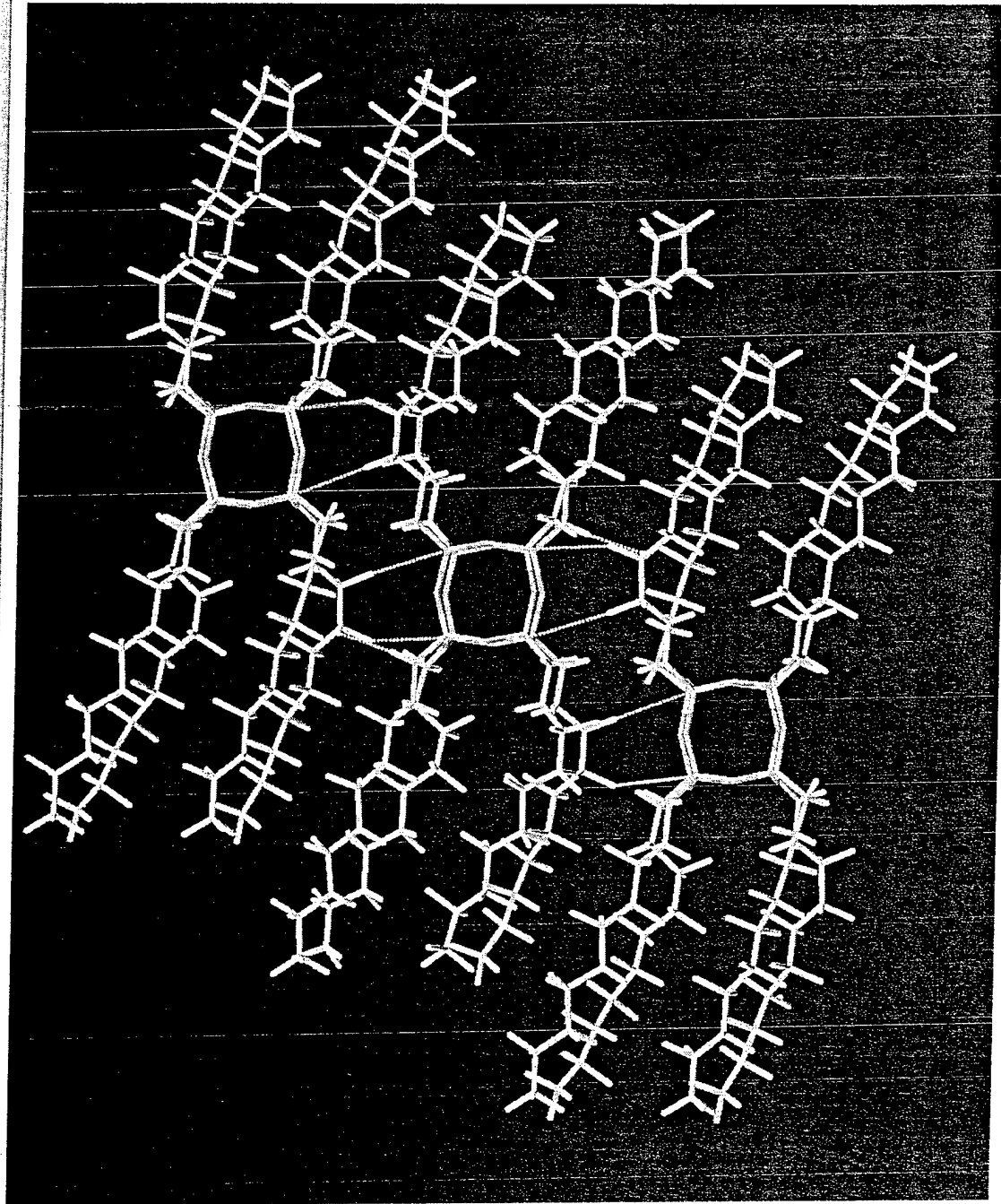
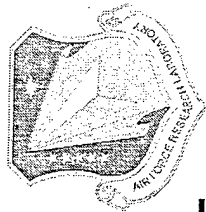
$$\rho = 2.05 \text{ g/mL}$$

$$M_w = 3193.45 \text{ g/mol}$$

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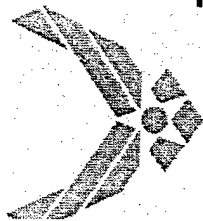
Fluorodecyl₈T₈



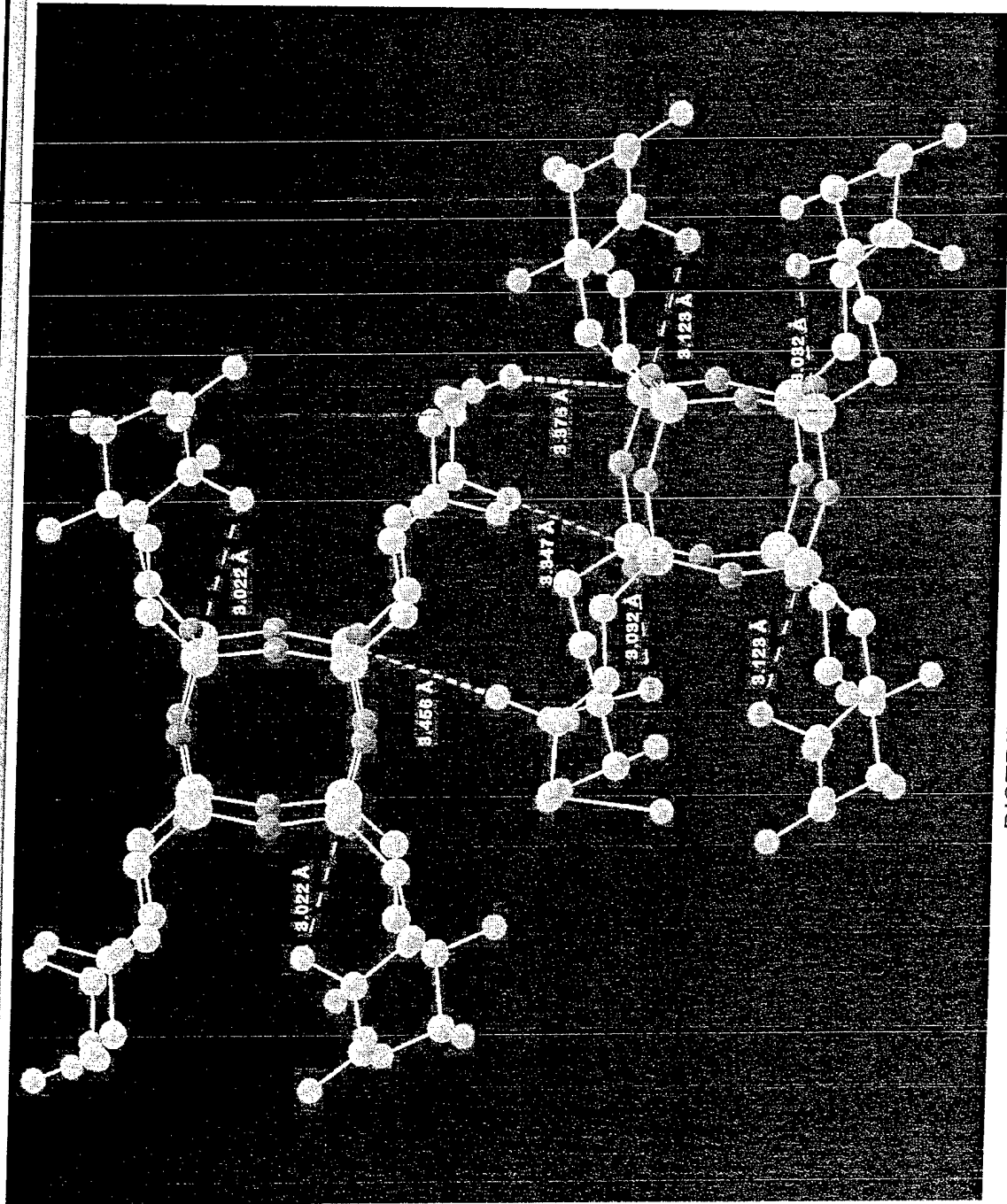
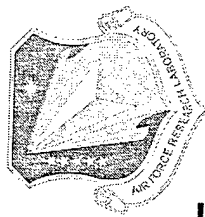
$$\rho = 2.06 \text{ g/mL}$$

$$M_w = 3993.54 \text{ g/mol}$$

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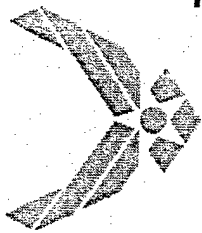


Fluorodecyl₈T₈

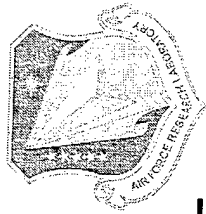


Inter- and intra-
molecular Si-F
contacts affect
crystal packing

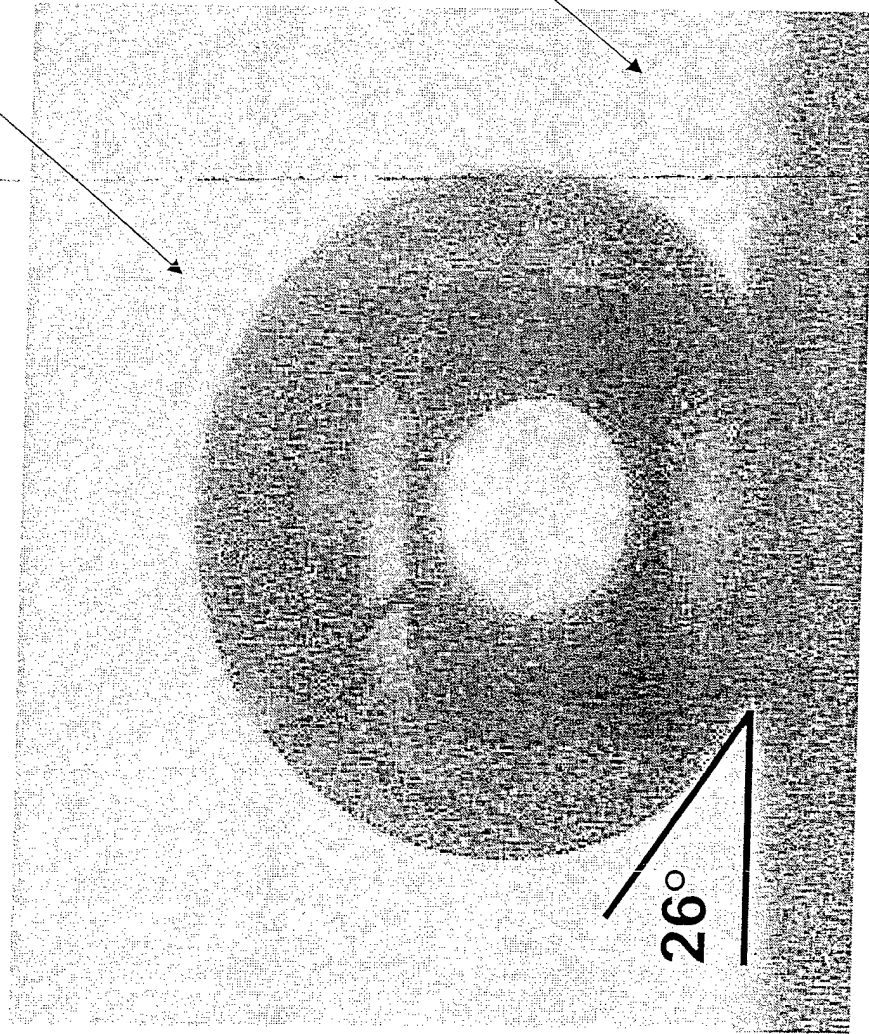
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Contact Angle of Water on Fluorodecyl POSS Surface



Drop of
 H_2O

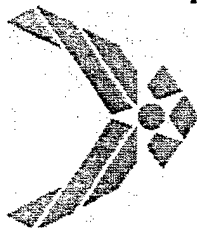


POSS
Coated
Surface

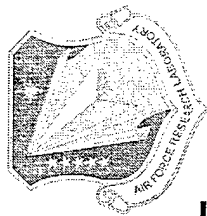
- Anti Icing surfaces
- Low Friction Surfaces

40° Higher than PTFE

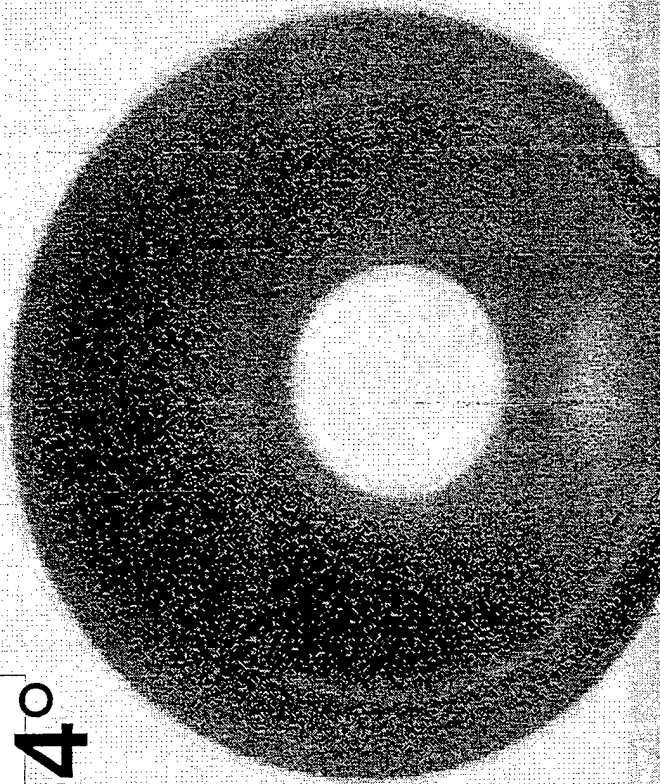
26°



Contact Angle of Water on Fluorodecyl POSS Surface

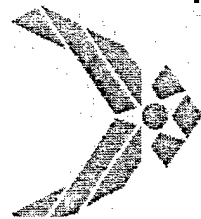


154°

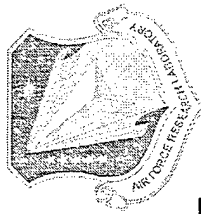


40° Higher than PTFE

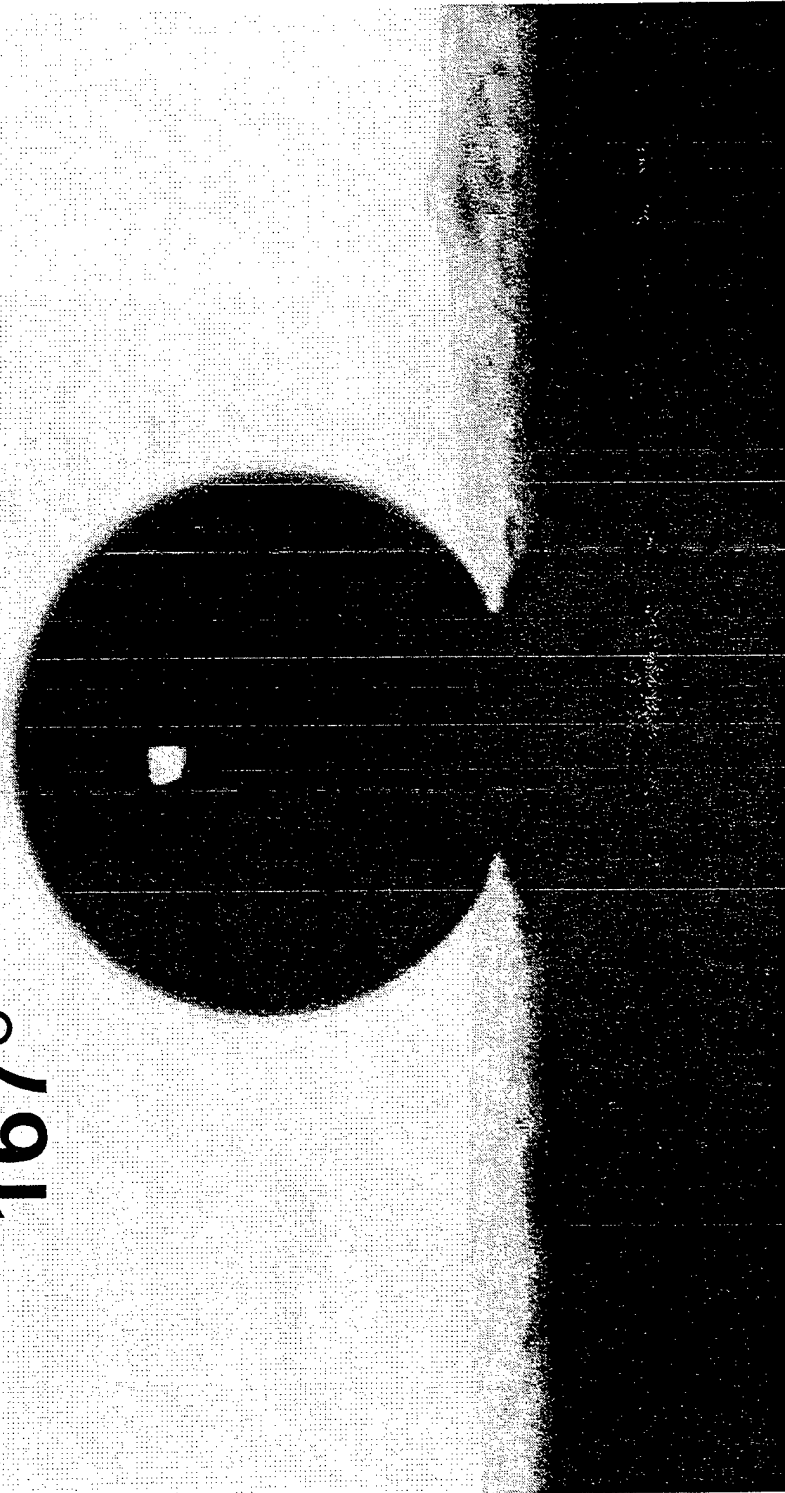
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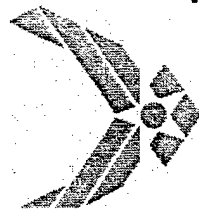
Contact Angle of Mercury on Fluorodecyl POSS Surface



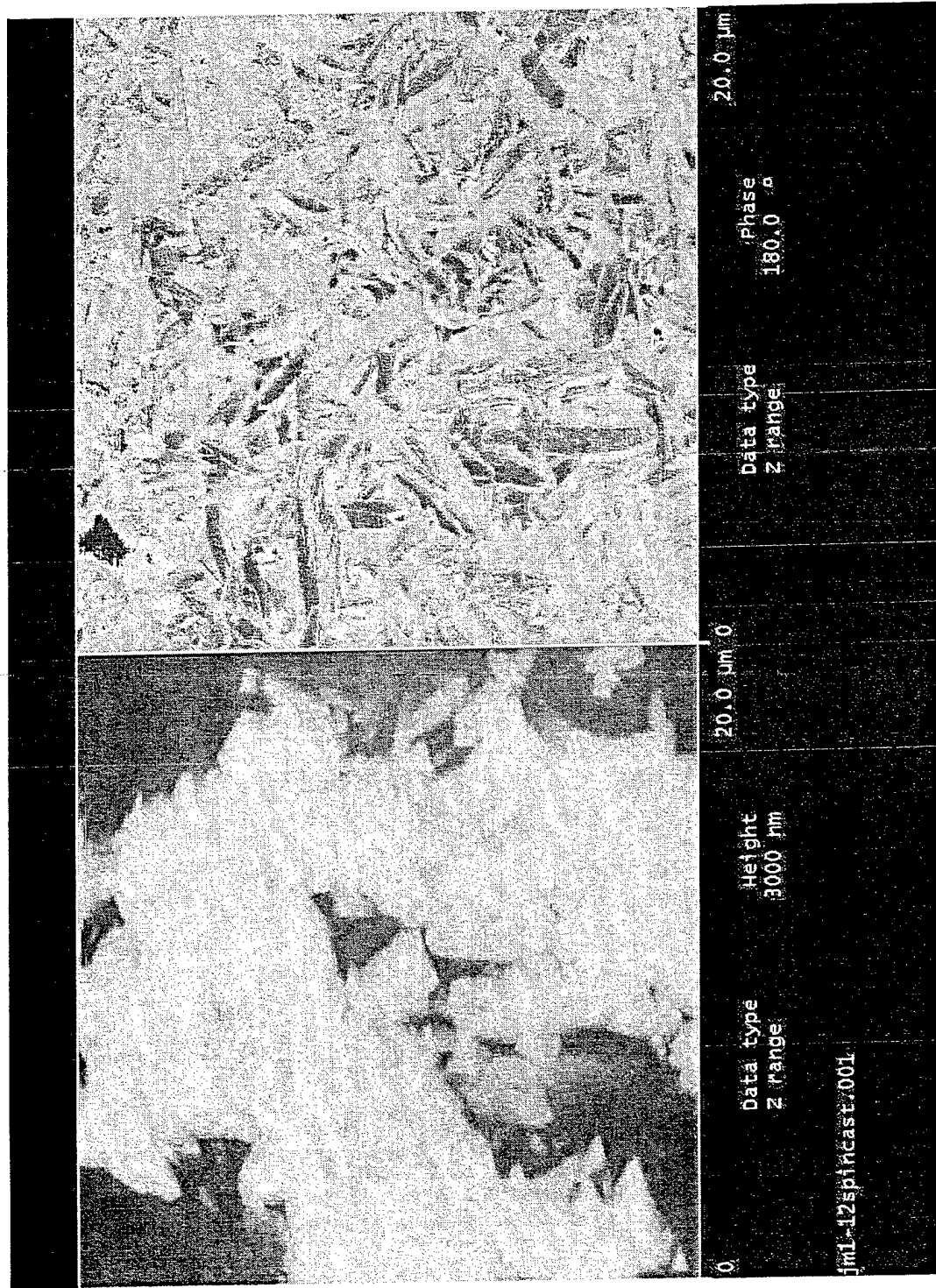
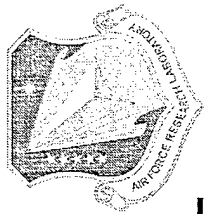
167°



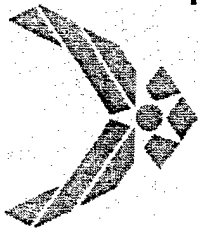
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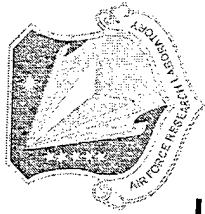
AFM Image of Spin-Cast Fluorodecyl₁₈T₈ Surface



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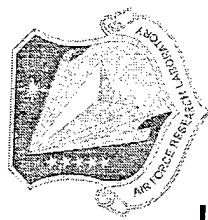
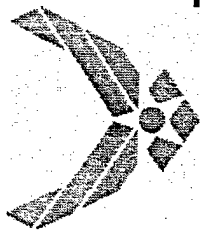
Surface Energy of Fluorosiloxanes



<u>Polymer</u>	<u>Surface Energy (mJ/m²)</u>
Poly(methylheptadecafluorodecylsiloxane)	7.0
Poly(methylnonafluorohexylsiloxane)	9.5
Poly(methyltrifluoropropylsiloxane)	13.6
Poly(dimethylsiloxane) (PDMS)	22.8
Poly(tetrafluoroethylene) (PTFE)	19.1

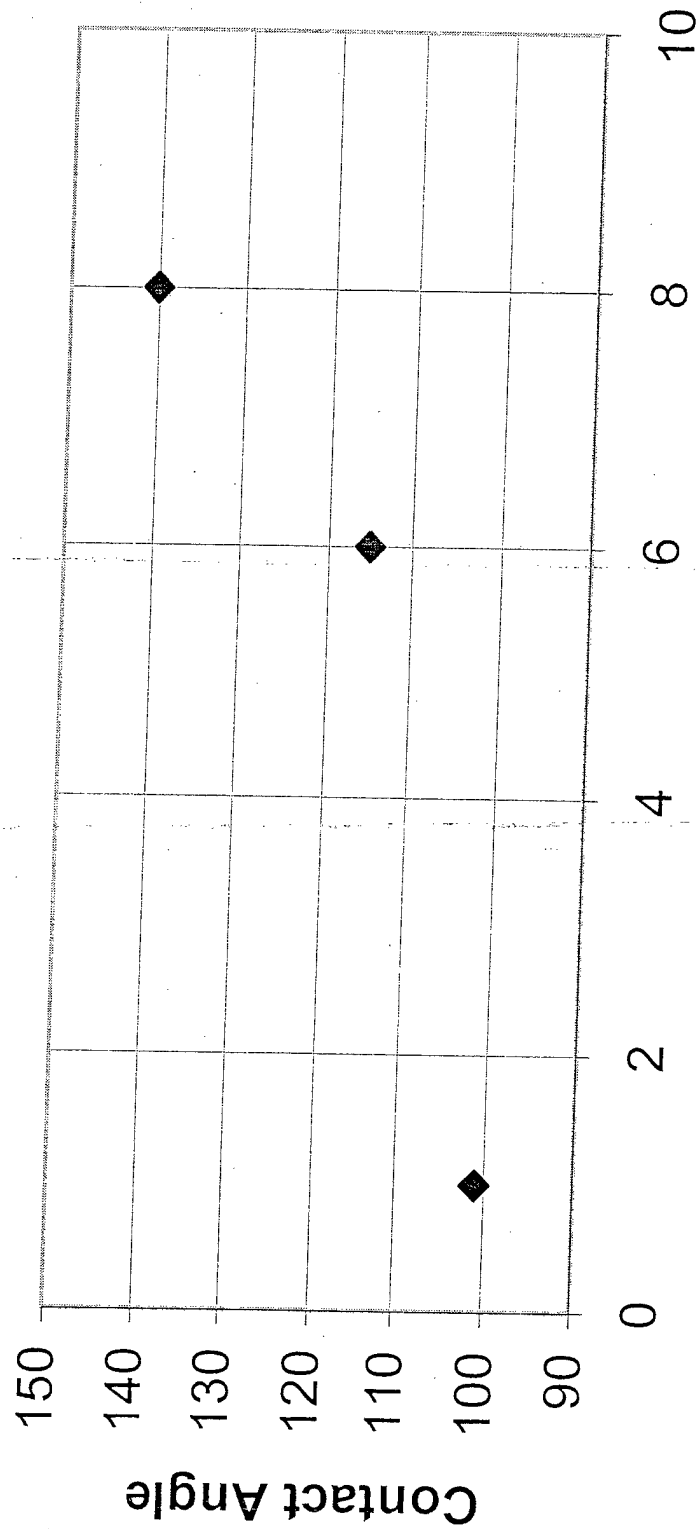
Maxson, M. T.; Norris, A. W.; Owen, M. J. "Fluorosilicones" In "Modern Fluoropolymers"; Scheirs, J. Ed.; J. Wiley & Sons: New York, 1997, pp 359-372.

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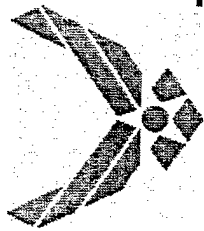


Contact Angle and Chain Length

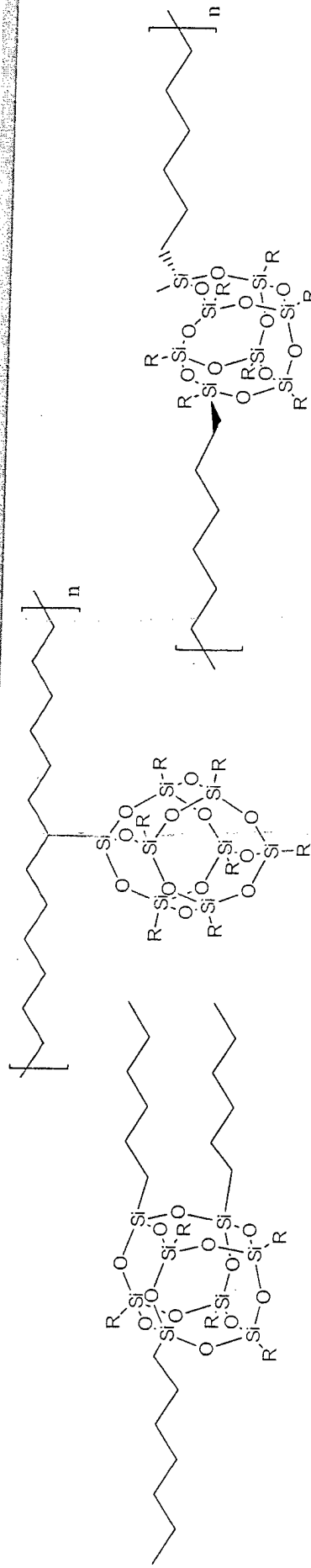
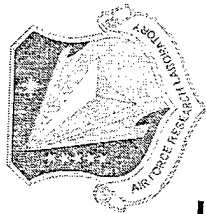
Chain Length vs. Contact Angle



Number of Fluorocarbon Atoms



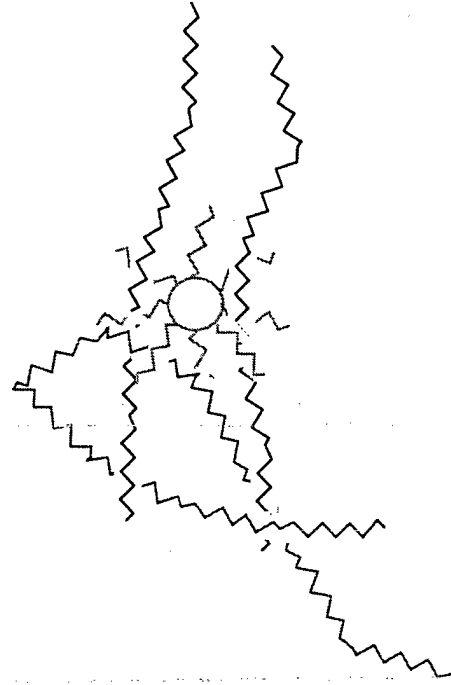
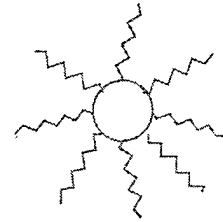
POSS Polymer Incorporation



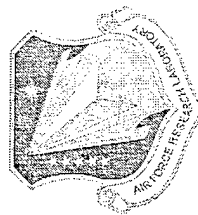
Cross-linker

POSS Pendant

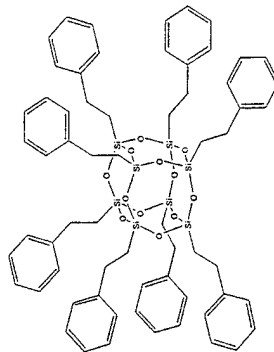
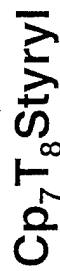
Bead Copolymer



POSS Blending



50 Wt % POSS Blends in 2 Million MW PS

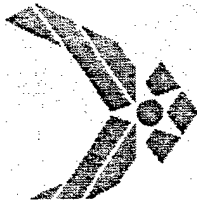


Immiscible POSS Crystallites

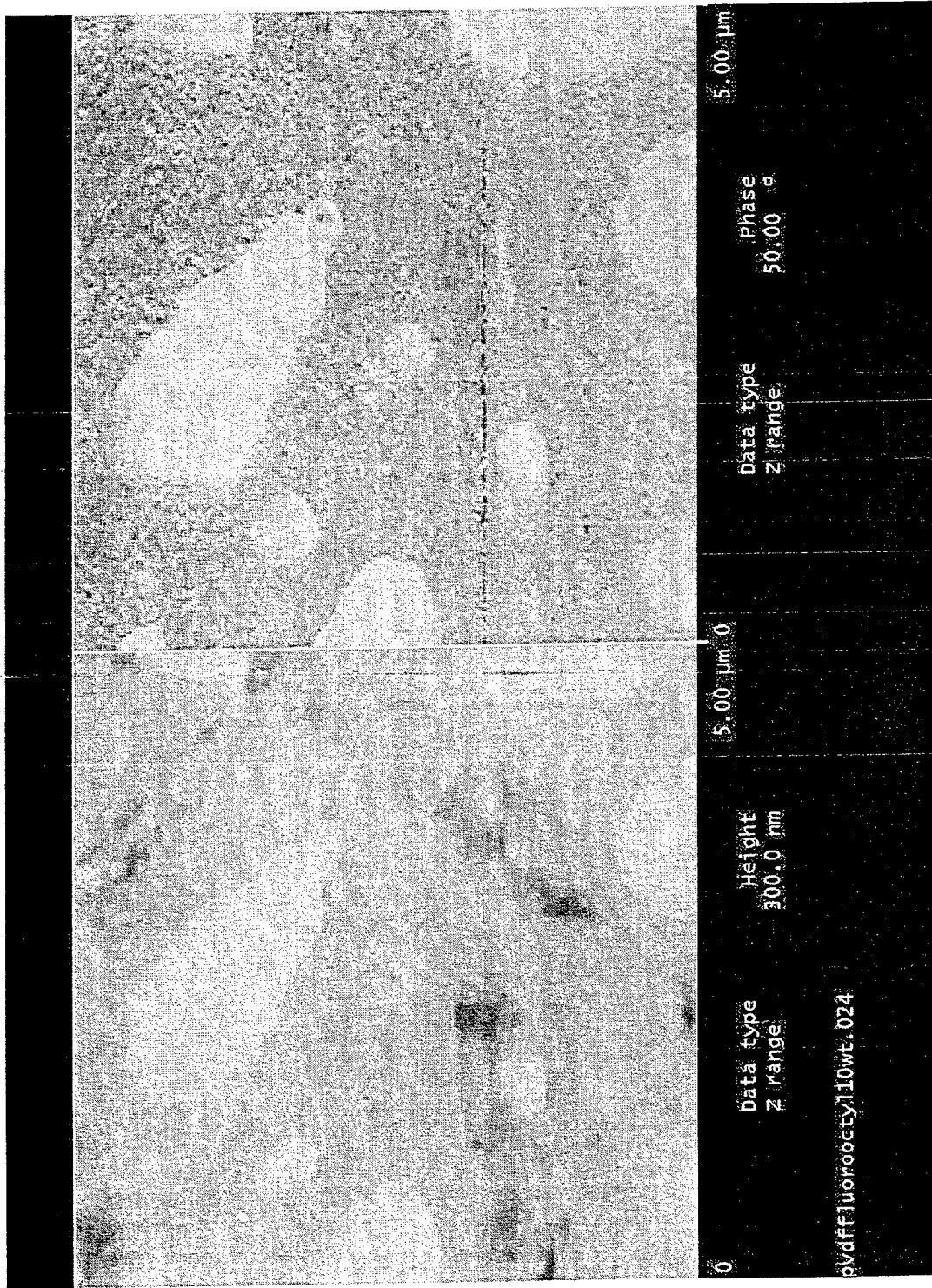
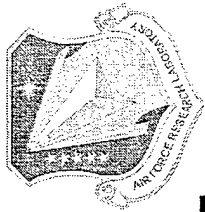
Complete Compatibility

Blanski, et al., *Polymer Preprints*, **2000**, 41(1): p. 585.

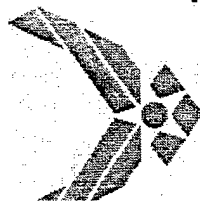
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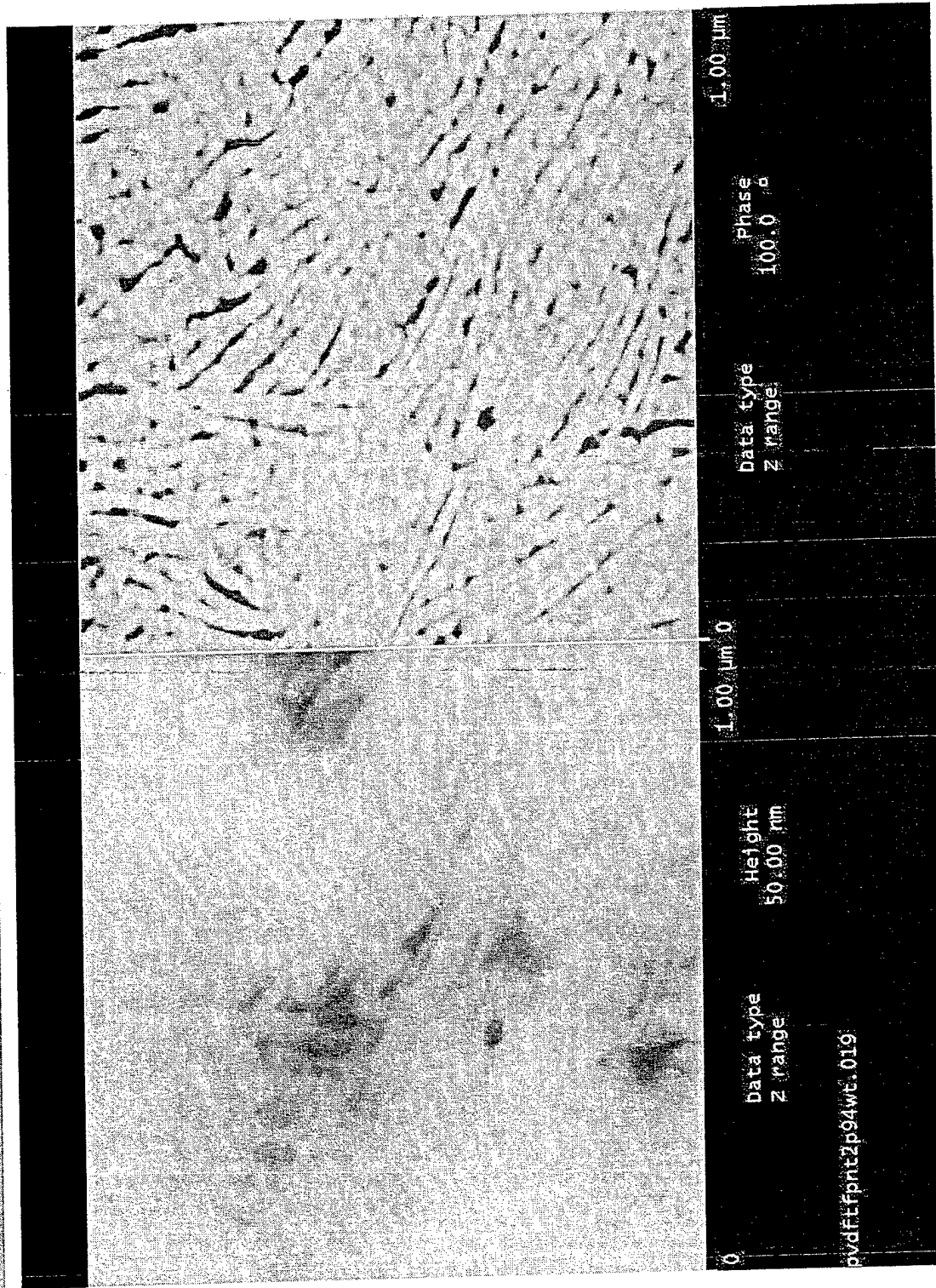
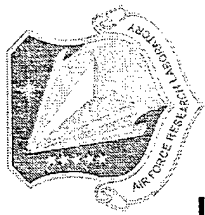
PVDF/Fluorooctyl₈T₈ POSS



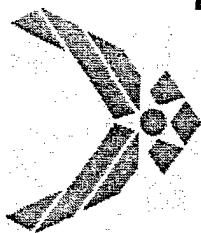
DISTRIBUTION A. Approved for public release; distribution unlimited.



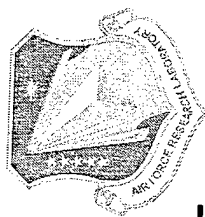
PVDF/Fluoropropyl_nT_n POSS



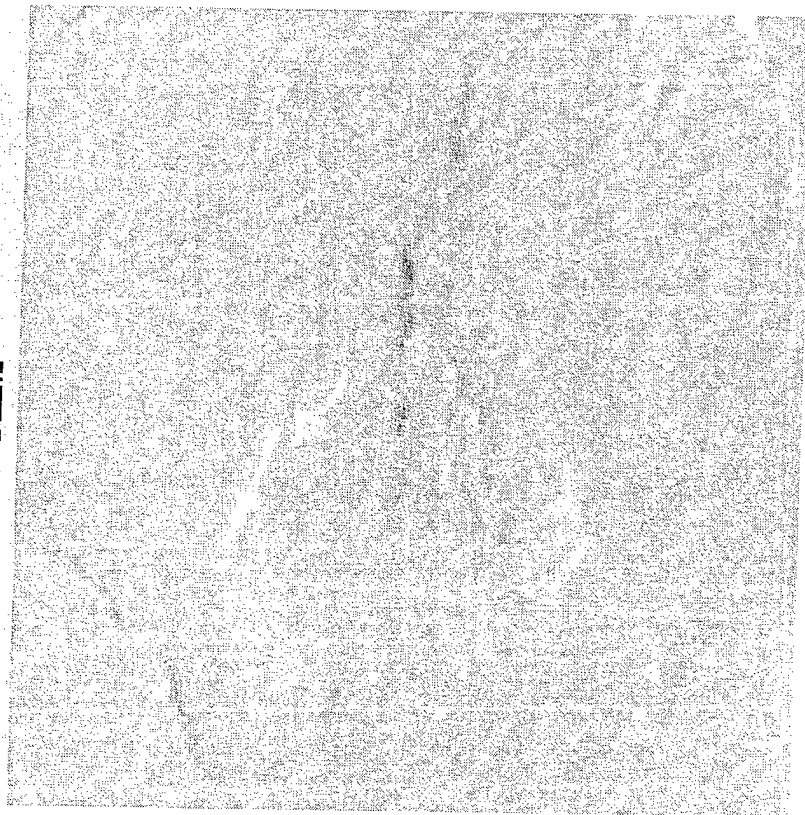
DISTRIBUTION A. Approved for public release; distribution unlimited.



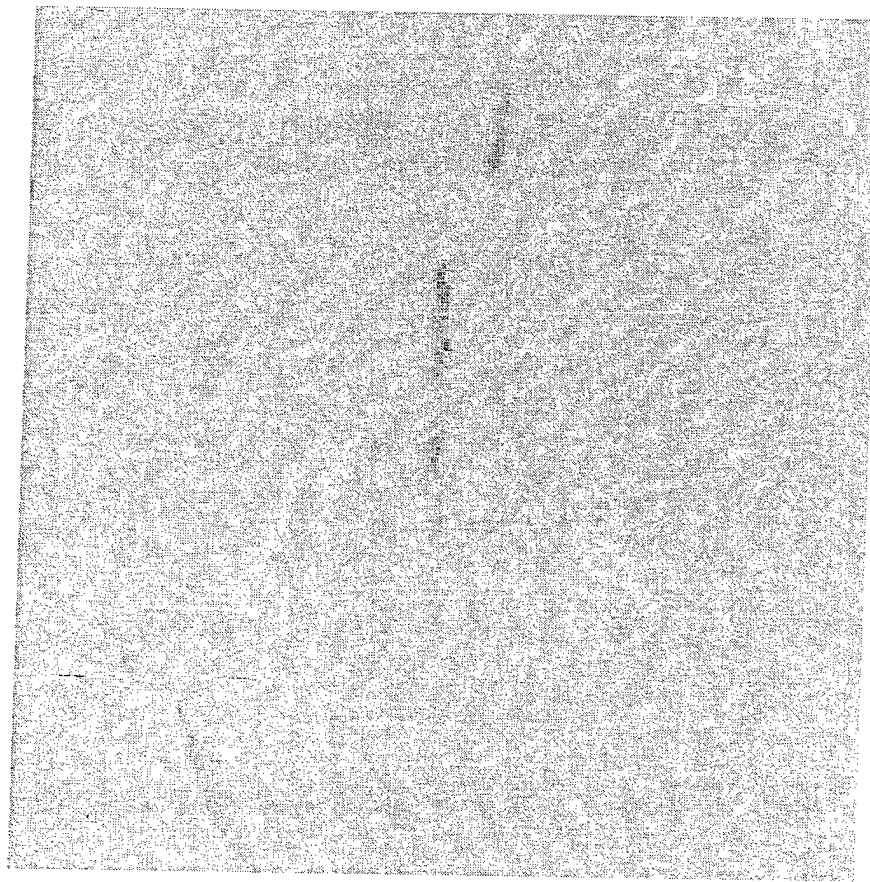
PVDF/Fluoropropyl_nT_n POSS



SEM



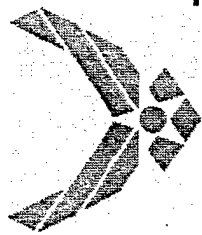
SEM Image



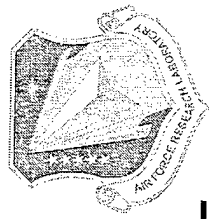
Carbon Map

SEM Image taken on cross-section of 1/4 inch thick sample bar.

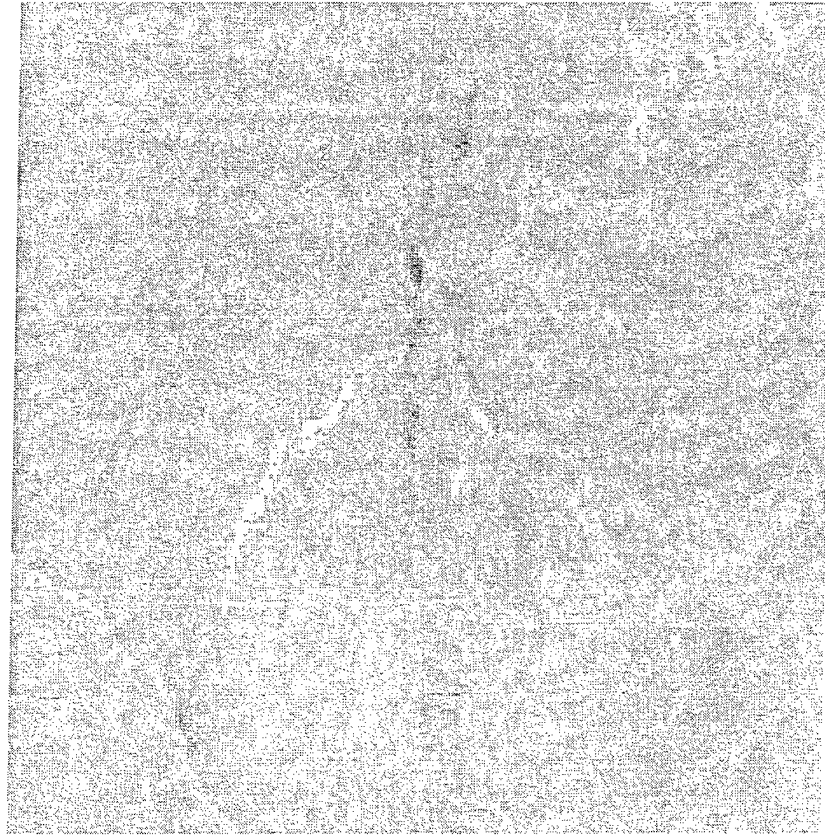
DISTRIBUTION A. Approved for public release; distribution unlimited.



PVDF/Fluoropropyl_nT_n POSS



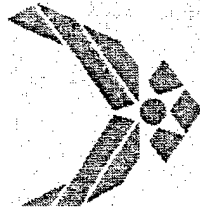
Fluorine Map



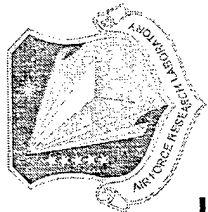
Silicon Map

Silicon map shows reasonable dispersion of POSS in polymer.

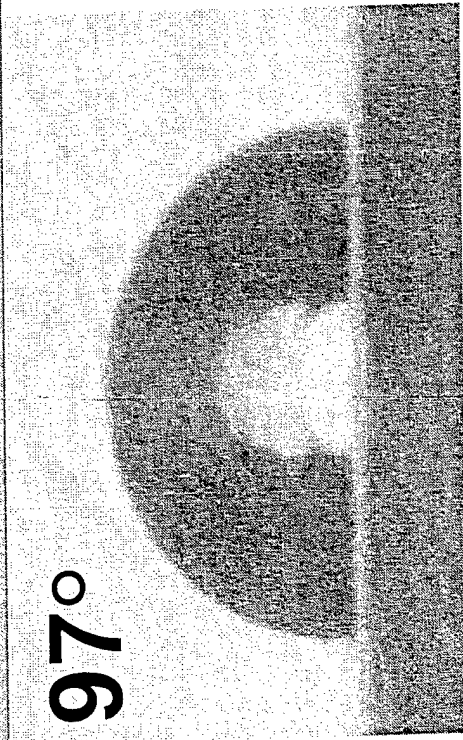
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Fluorinated Ethylene/Propylene

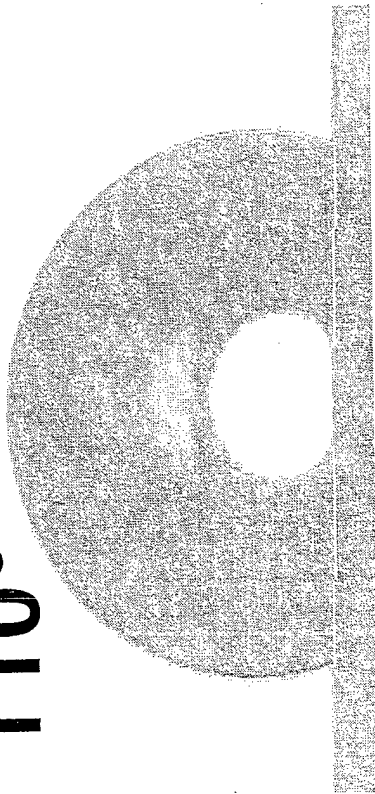


97°



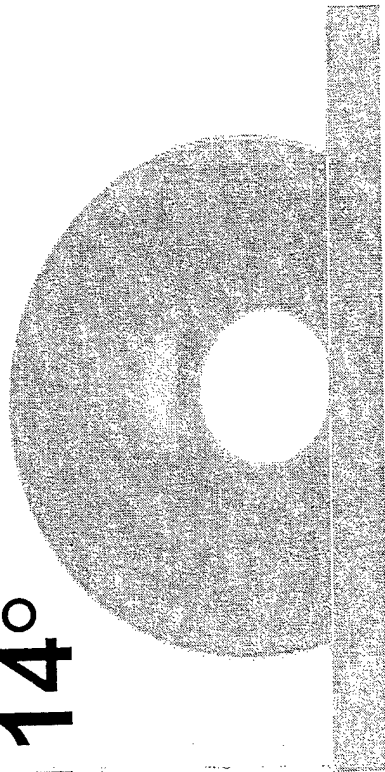
FEP

110°



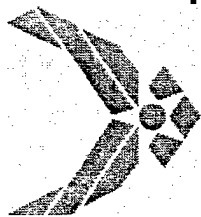
15% FO₈T₈

114°

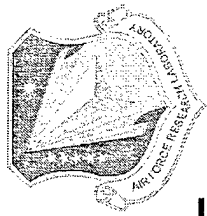


15% FD₈T₈

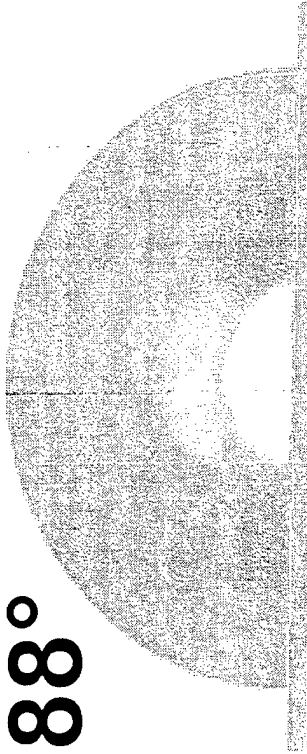
DISTRIBUTION A. Approved for public release; distribution unlimited.



Poly(chlorotrifluoroethylene)



88°



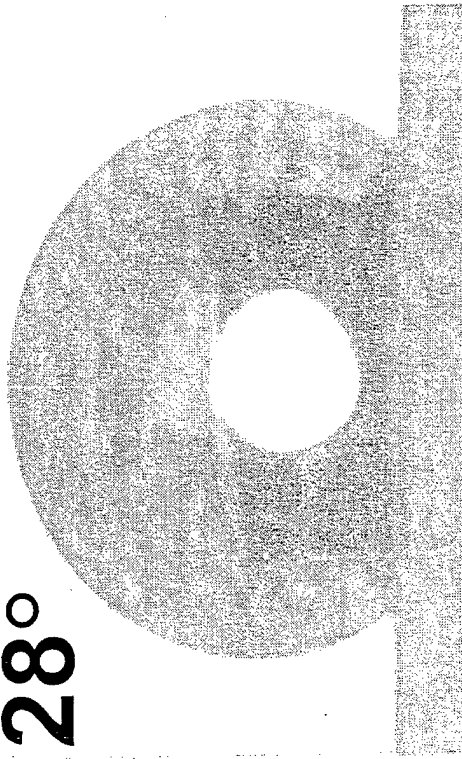
PCTFE

108°



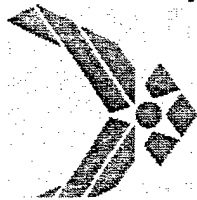
10% FO₈T₈

128°

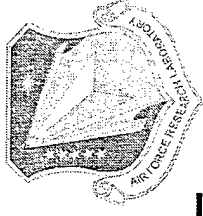


10% FD₈T₈

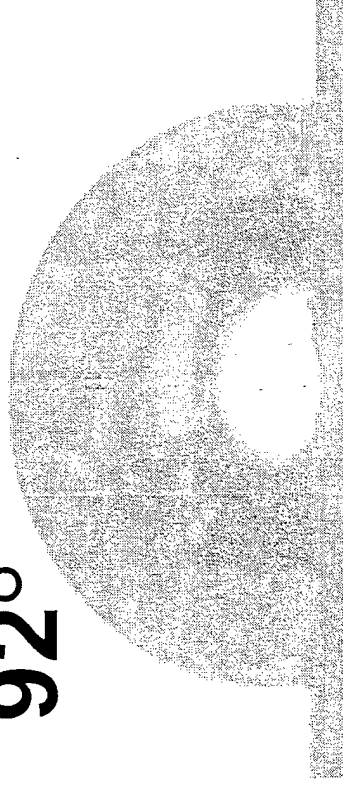
DISTRIBUTION A. Approved for public release; distribution unlimited.



Amorphous FEP



92°



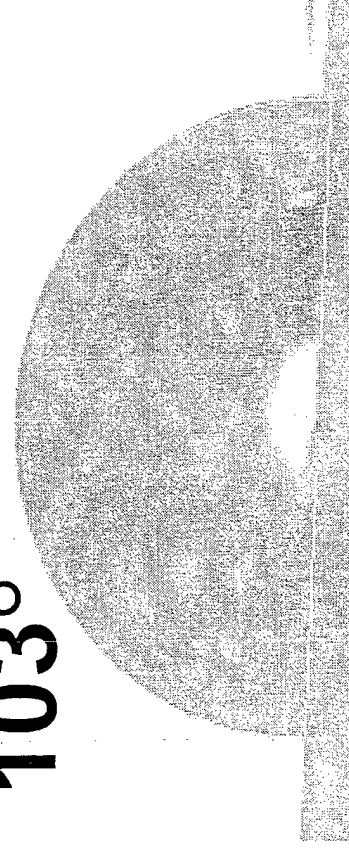
AFEP

100°



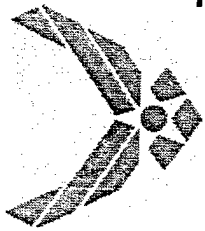
AFEP with 10% FO₈T₈

103°

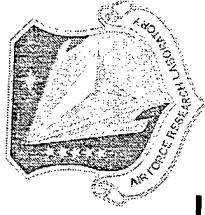


AFEP with 10% FD₈T₈

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Water Contact Angle



Polymer	No POSS	FO ₈ T ₈	FD ₈ T ₈
PCTFE	88°	108°	128°
FEP	97°	110°	114°
Amor. FEP	92°	100°	103°

Fluoropropyl POSS (FP_nT_n)

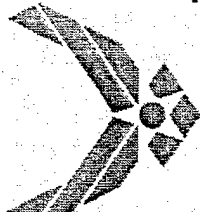
Fluorooctyl POSS (FO₈T₈)

Fluorodecyl POSS (FD₈T₈)

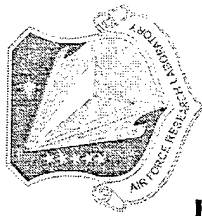
101°

115°

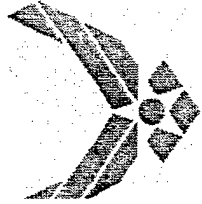
154°



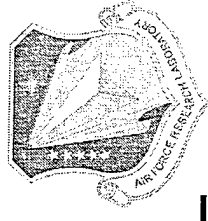
Summary



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Acknowledgements

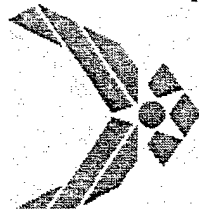


Assistance from others at AFRL:

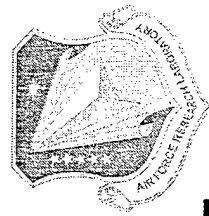
Crystal Structures
SEM Images
SEM Images
AFM Images

Ashwani Vij
Marietta Fernandez
Erik Weber
Brian Moore

Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate

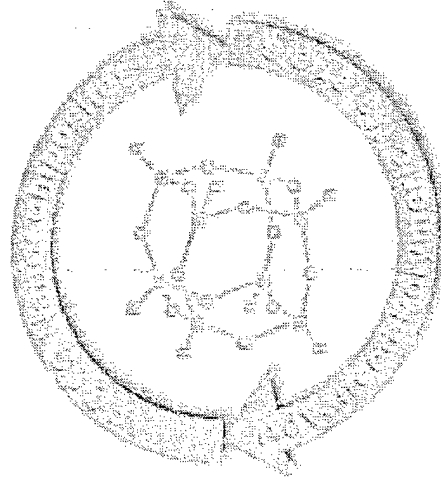


Acknowledgements



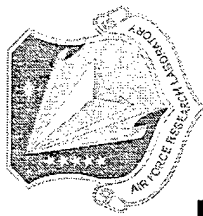
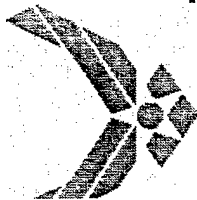
The Polymer Working Group at Edwards Air Force Base is:

Maj Connie Schlaefer
Mr. Pat Ruth
Dr. Sandra Tomczak
Mr. Brian Moore
Dr. Brent Viers
Dr. Darrell Marchant
Lt Will Cooper
Mr. Scott Barker



Dr. Shawn Phillips
Lt Amy Palacek
Dr. Rusty Blanski
Dr. Joe Mabry
Mrs. Sherly Largo
Dr. Tim Haddad
Lt Laura Moody

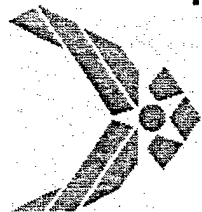
Financial Support:
Air Force Office of Scientific Research
Air Force Research Laboratory, Propulsion Directorate



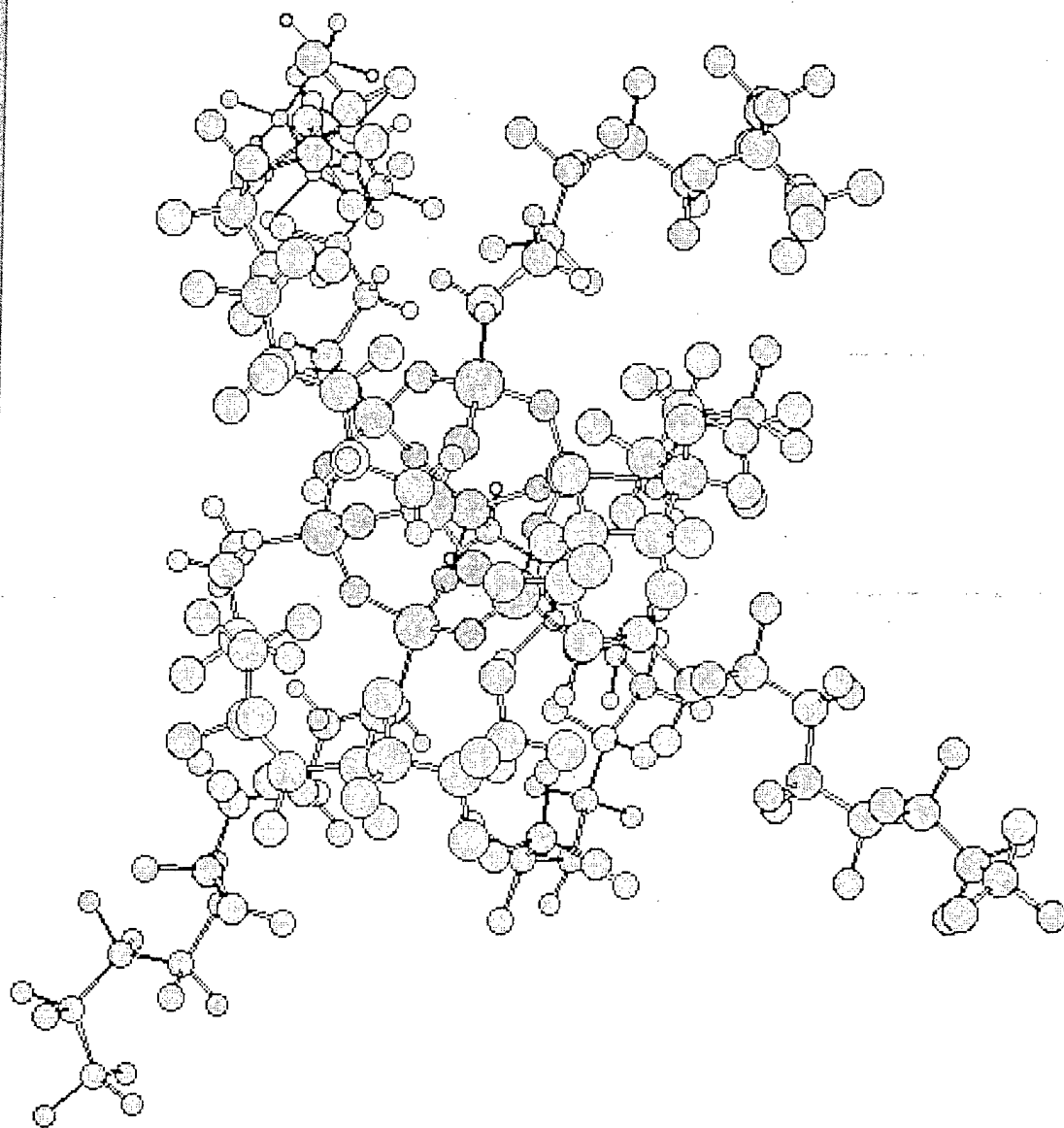
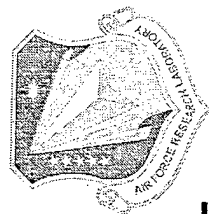
Backup Slides

PAS-03-061

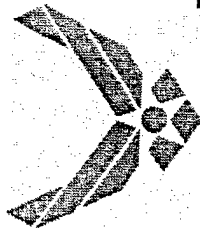
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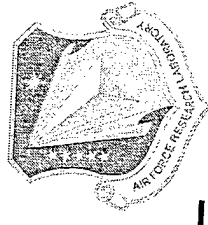
Gas Phase Model of Fluorodecyl₈T₈



DISTRIBUTION A. Approved for public release; distribution unlimited.

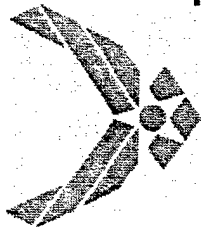


Density

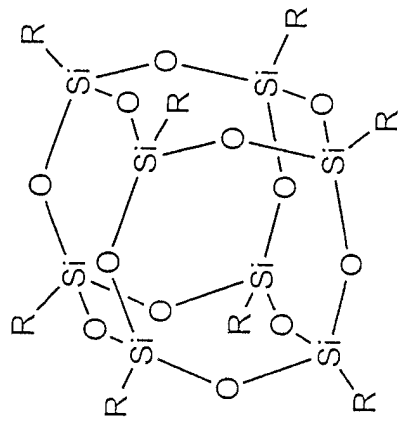
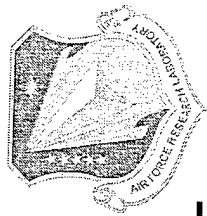


<u>Compound</u>	<u>Density (g/mL)</u>
• PVDF	1.75-1.78
• PCTFE	2.08-2.19
• FEP	2.12-2.17
• Fluoropropyl POSS	1.59
• Fluorohexyl POSS (crystal)	1.86 (1.98)
• Fluorooctyl POSS (crystal)	1.88 (2.05)
• Fluorodecyl POSS (crystal)	1.95 (2.06)

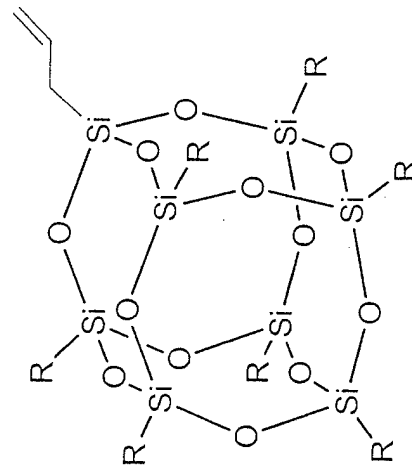
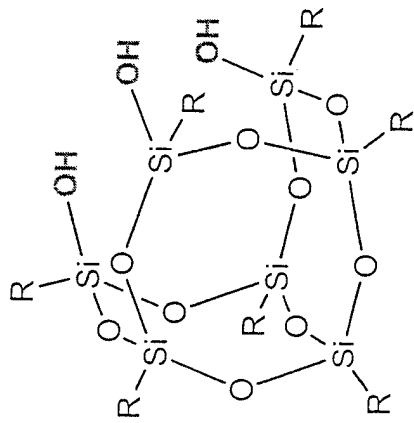
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Fluorinated POSS Trisilanol



$\xrightarrow[\text{reflux}]{\text{Et}_4\text{NOH}}$

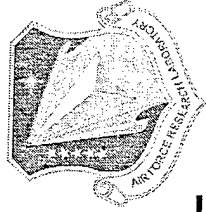
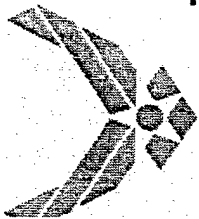


$\xrightarrow{\text{Et}_3\text{N}}$

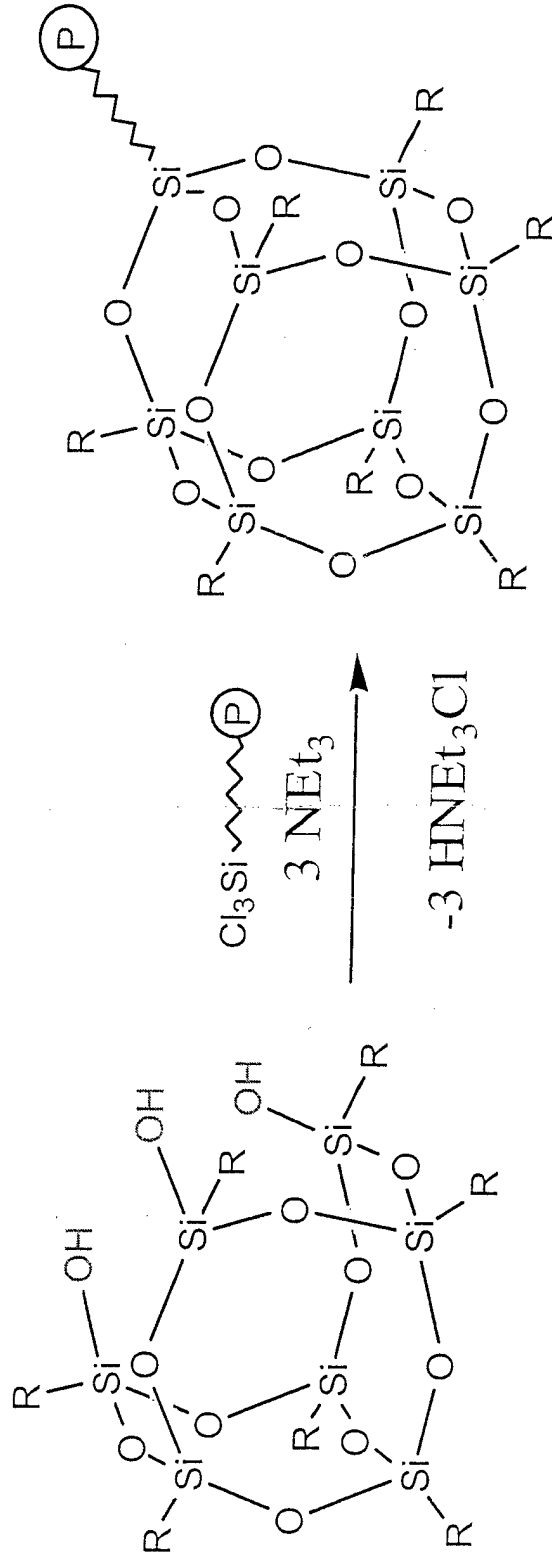


(or other chlorosilanes)

DISTRIBUTION A. Approved for public release; distribution unlimited.



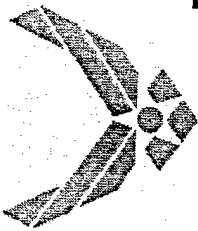
POSS Macromers for Nanocomposites



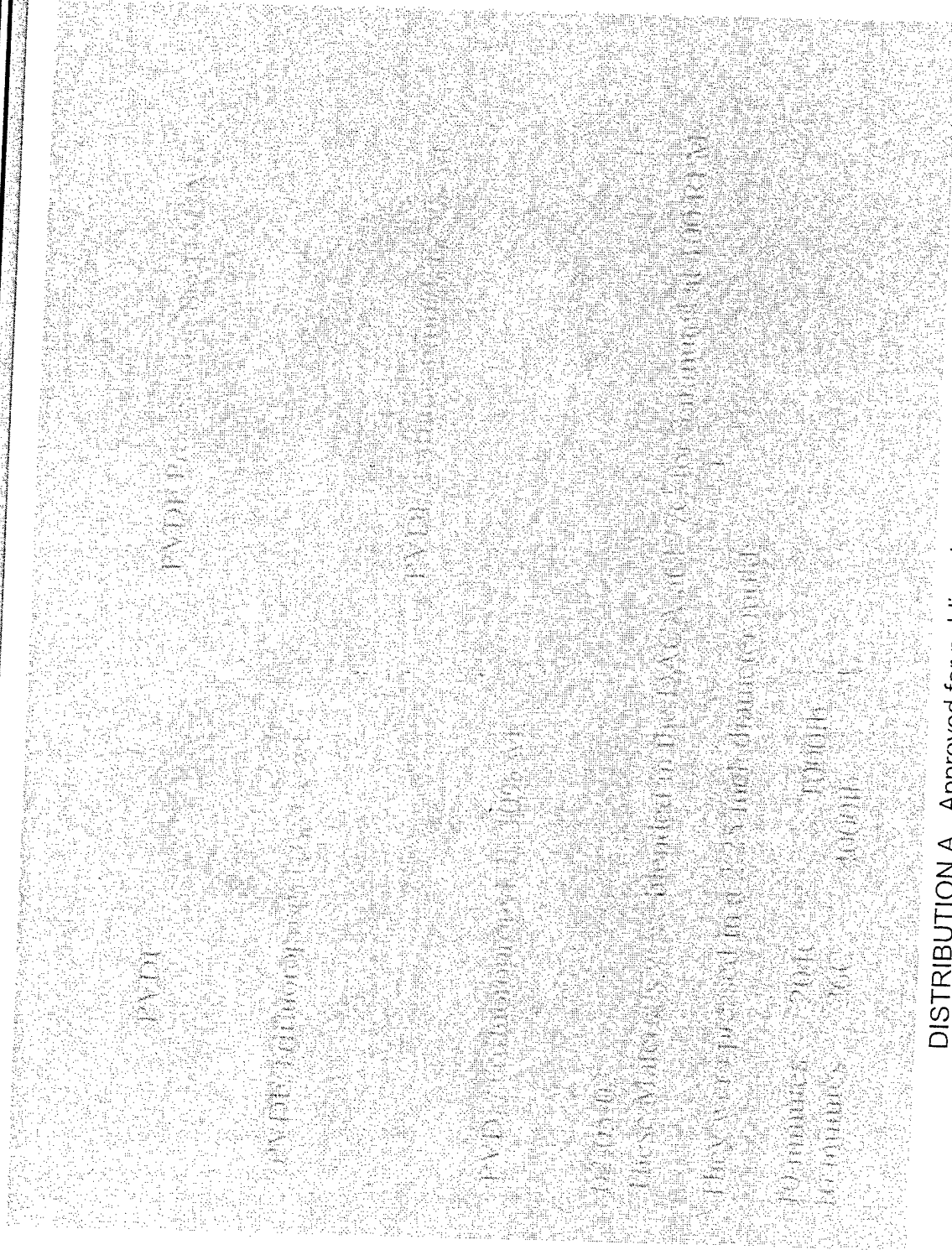
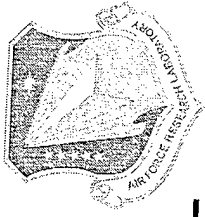
POSS-based macromers are available through either **Gelest** or **Aldrich**
POSS technology is commercialized by **Hybrid Plastics** in Fountain Valley CA

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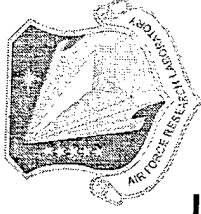
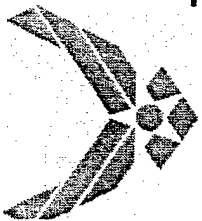
DISTRIBUTION A. Approved for public release; distribution unlimited.



PVDF Fluoropropyl_nT_n Blends



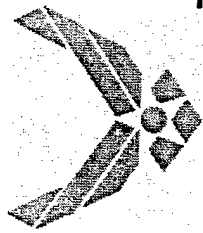
DISTRIBUTION A. Approved for public release; distribution unlimited.



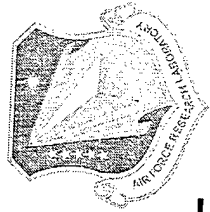
POSS Siloxanes

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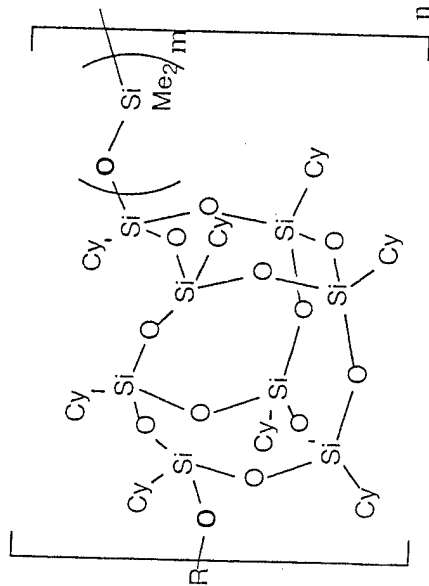
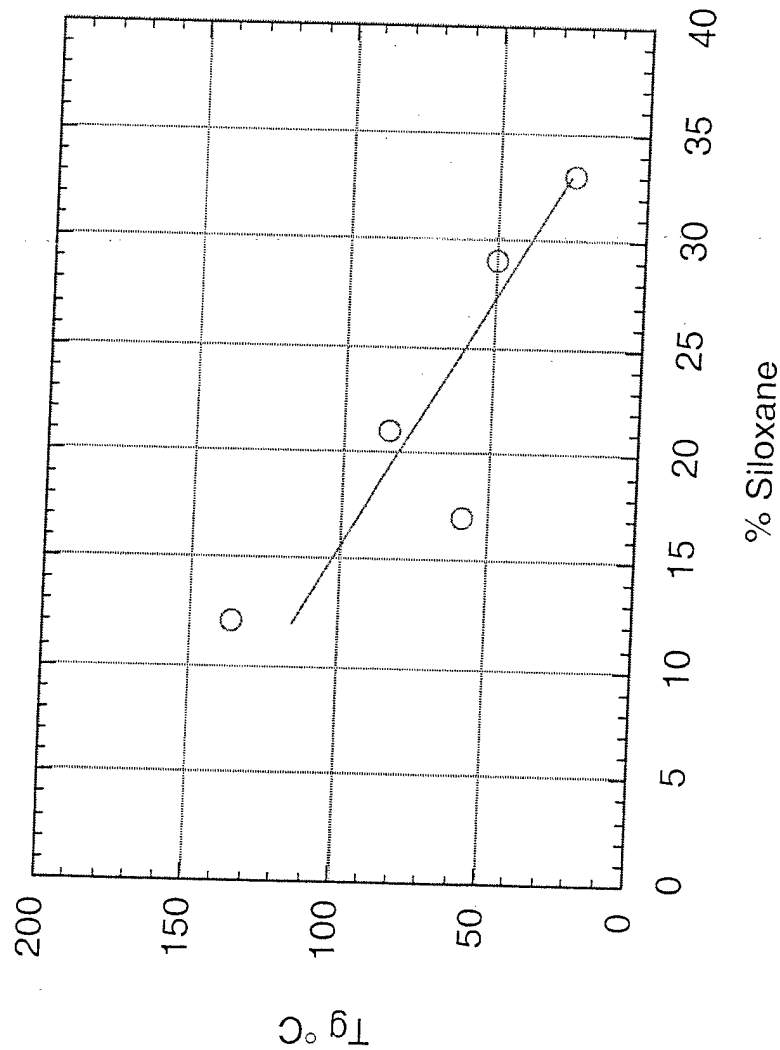
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Tg's For Bead Siloxane Copolymers



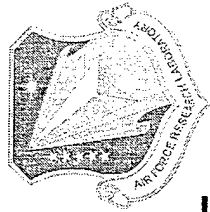
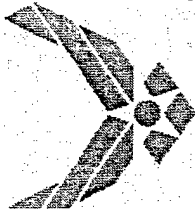
Glass Transition vs % Siloxane



POSS Bead acts as a hard segment

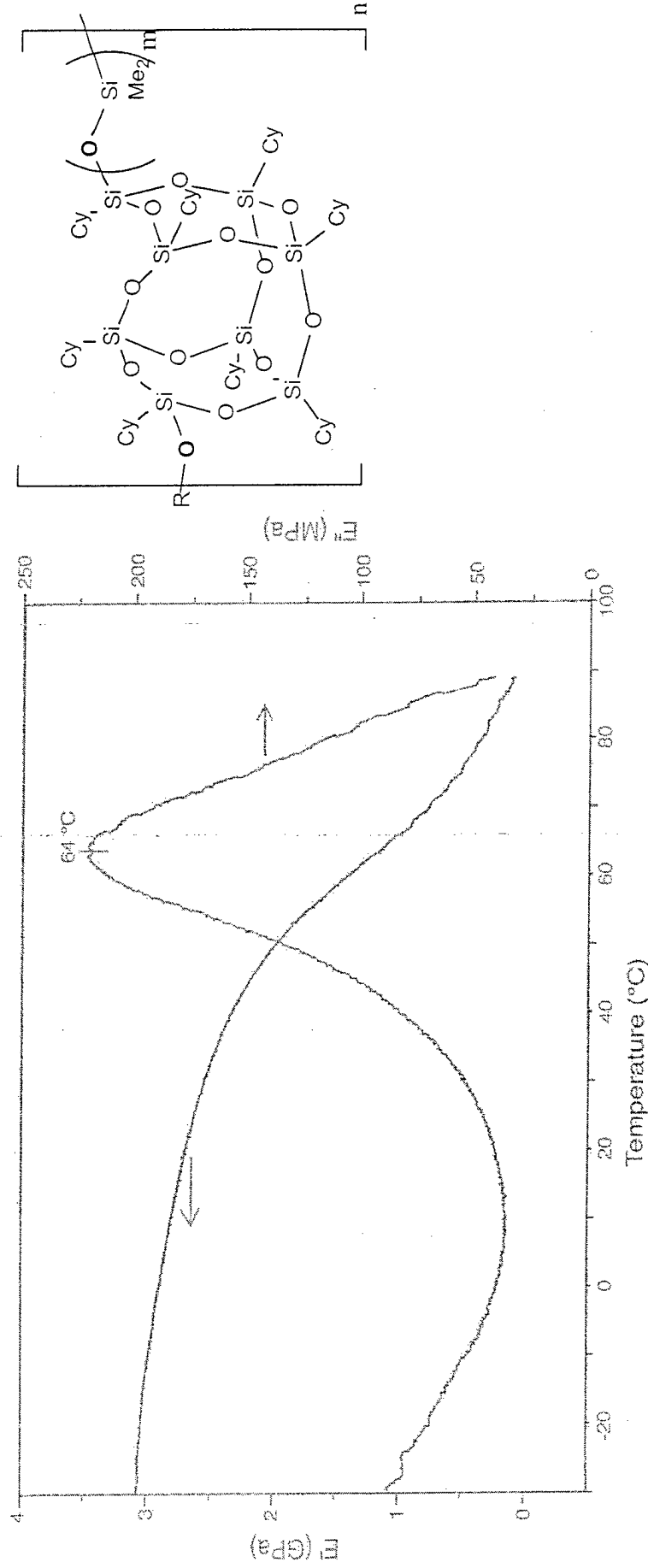
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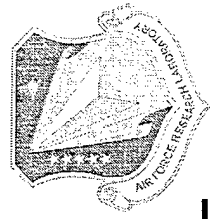
POSS Siloxanes

- Copolymers with low softening temperatures can be molded into bars.
- Dynamic mechanical analysis reveals a T_g (64°C).

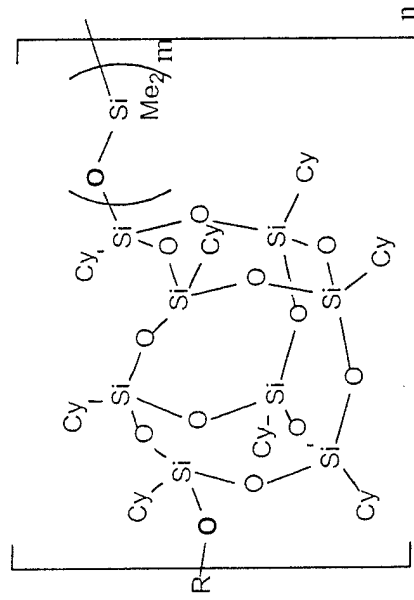


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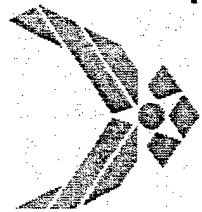
DISTRIBUTION A. Approved for public release; distribution unlimited.



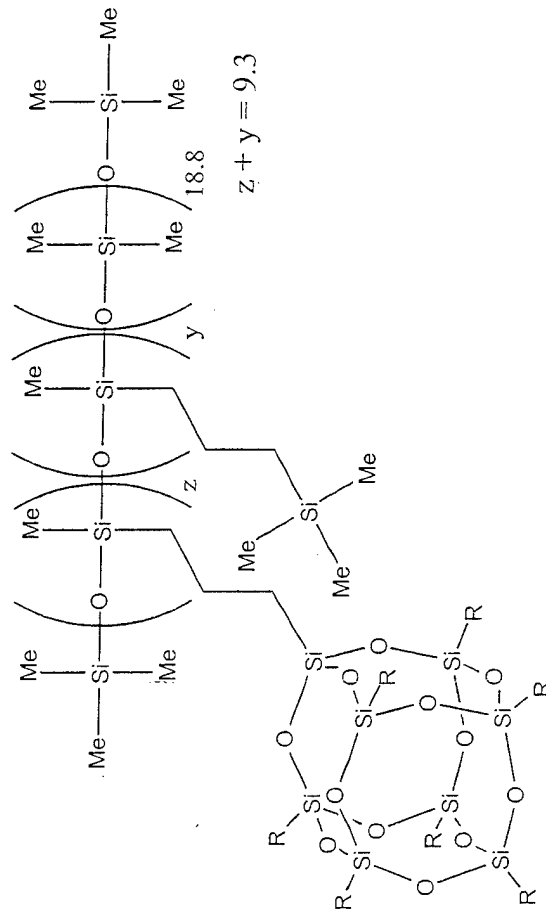
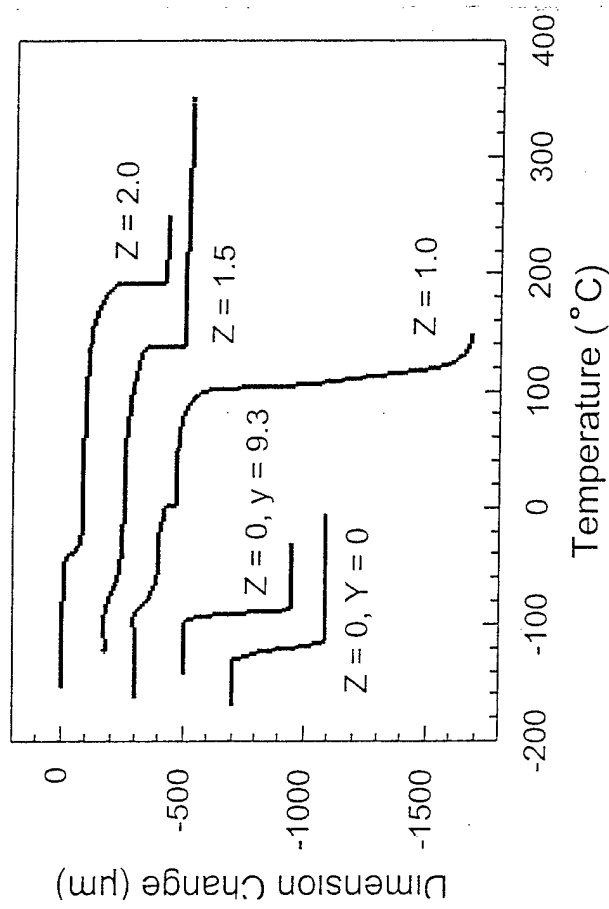
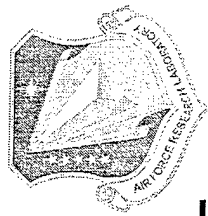
The POSS/Siloxane copolymers with four or more Si-O repeat units in the siloxane segment have softening temperatures well below the decomposition temperatures.



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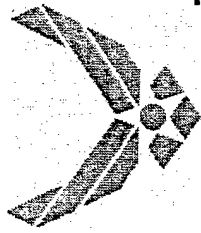


TMA of Pendent POSS-Siloxanes

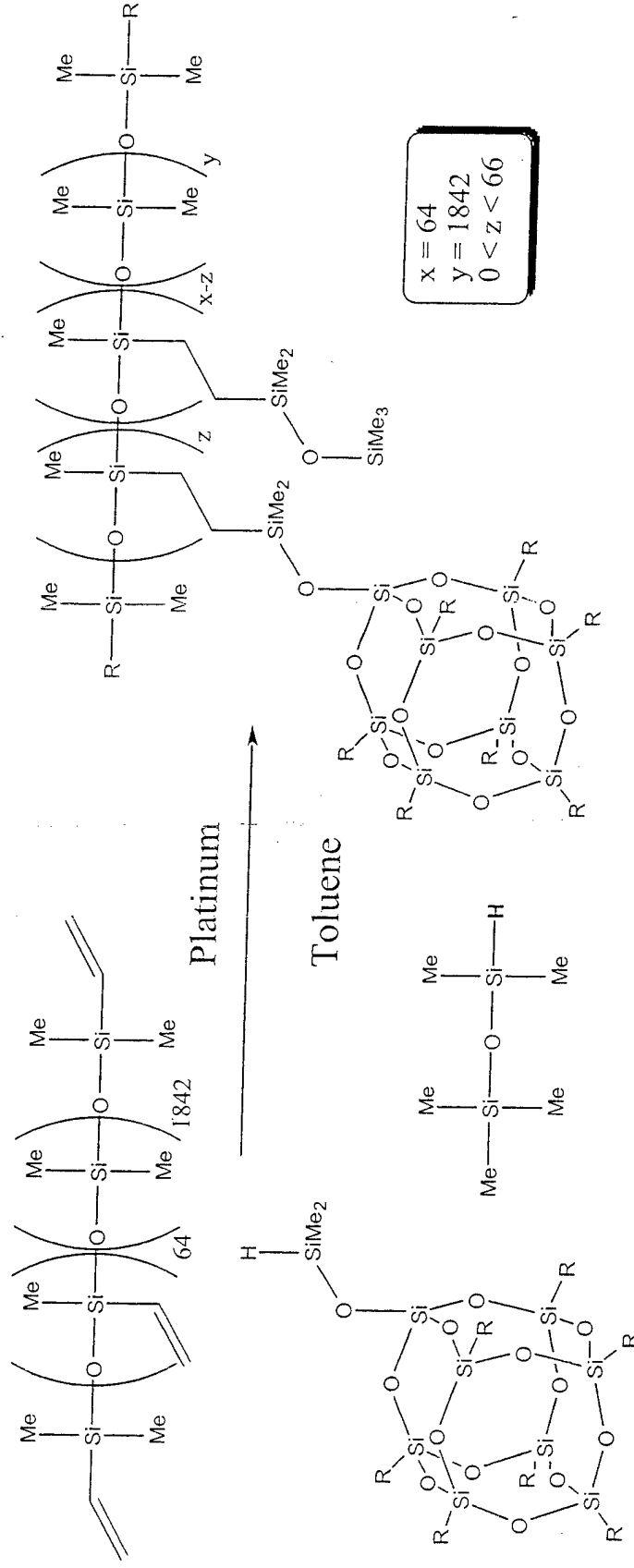
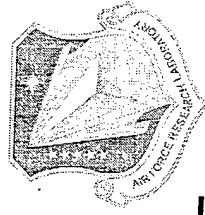


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Hydrosilation to High MW PDMS

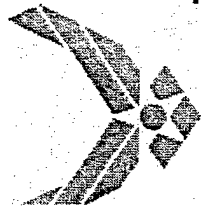


There are about 7 POSS-
macromers per PDMS chain

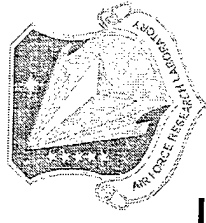
Used 5 weight % POSS

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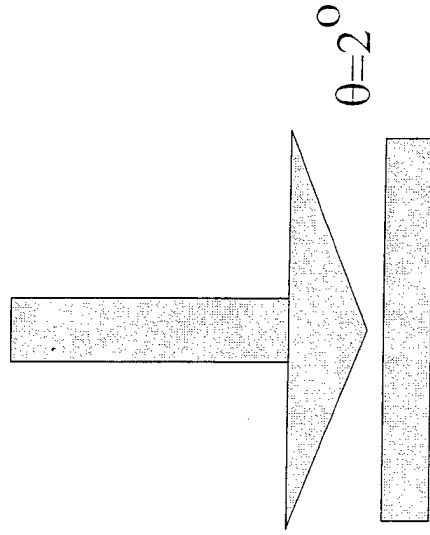
Experimental Setup for Rheology



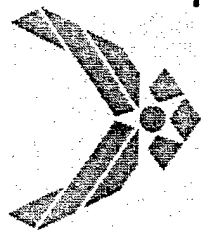
- 25 mm diameter cone-and plate with cone angle of 2° was used.
- The strain amplitude γ_o is 1% and angular frequency ω is 2π per second.
- The temperature is ramped from - 60°C to 70°C with a rate of $2^\circ\text{C}/\text{min}$.

$$\gamma(\omega) = \gamma_o \sin(\omega t)$$

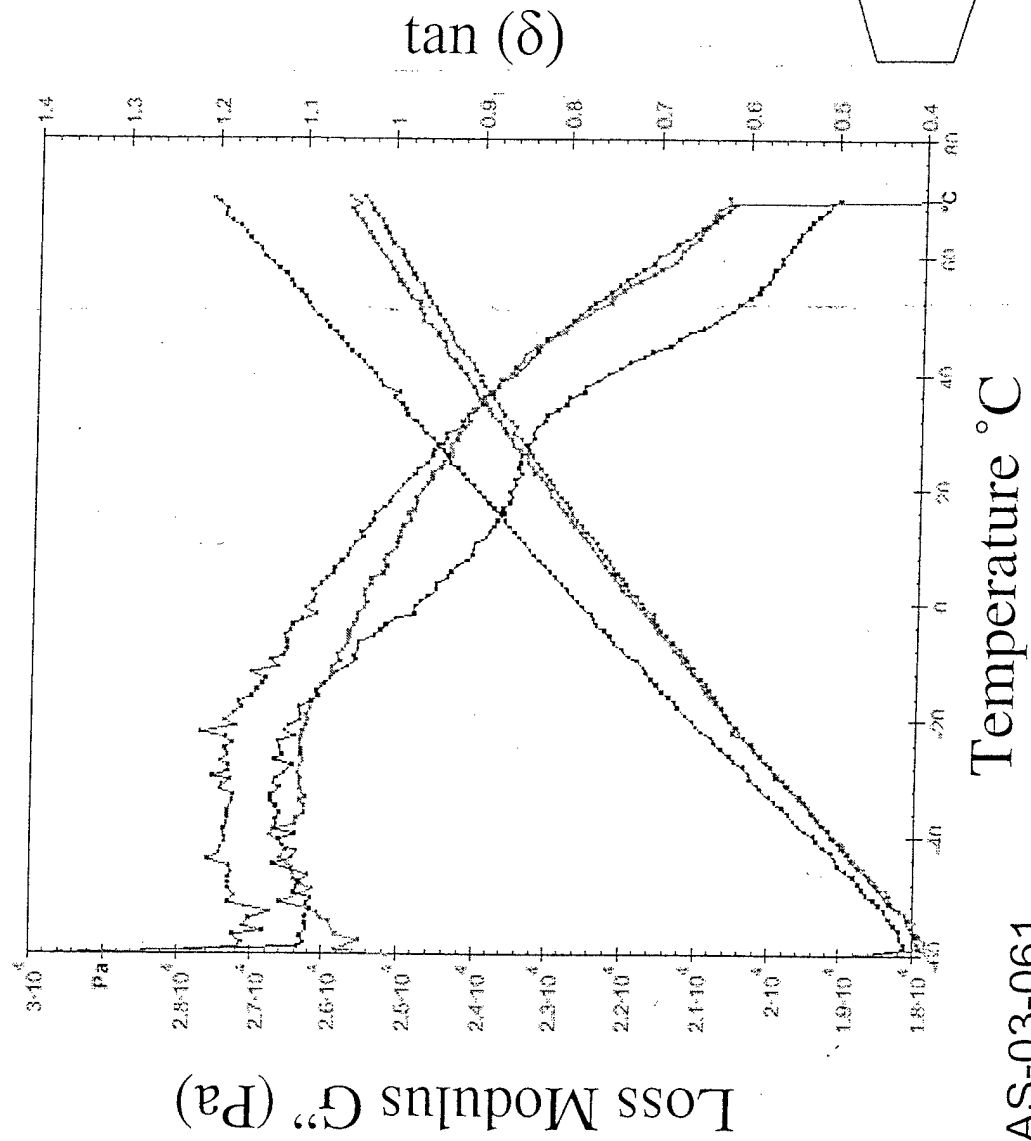
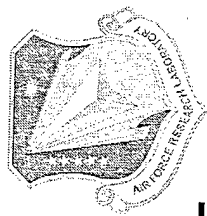
$$\omega = 2\pi (\text{sec}^{-1})$$



The loss modulus G'' and $\tan \delta = G''/G'$ were obtained as a function of temperature.



Comparison of Three T8-POSS Macromers

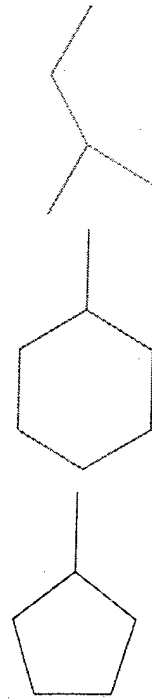
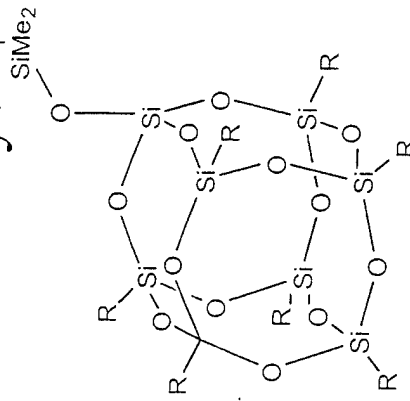


PDMS + 5 wt % POSS

Blue = cyclopentyl

Red = cyclohexyl

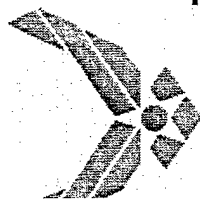
Purple = isobutyl



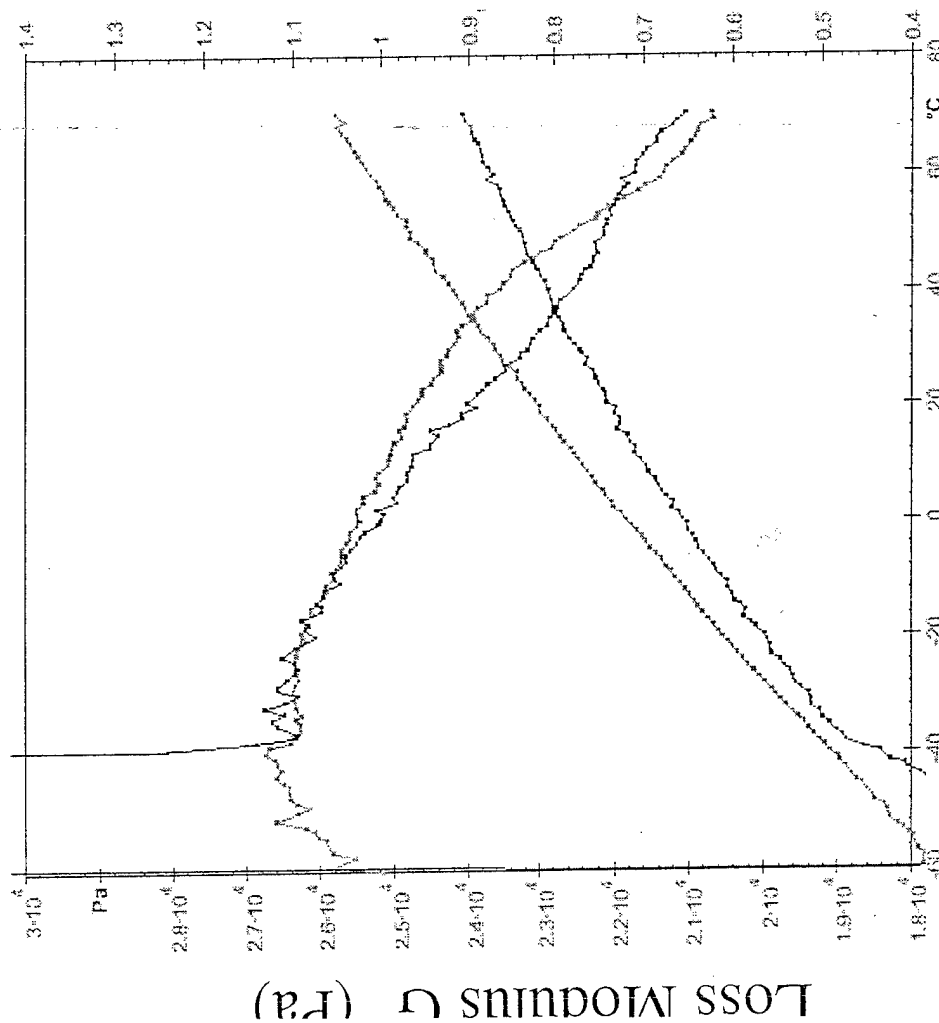
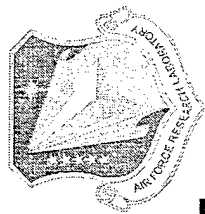
PAS-03-061

Temperature °C

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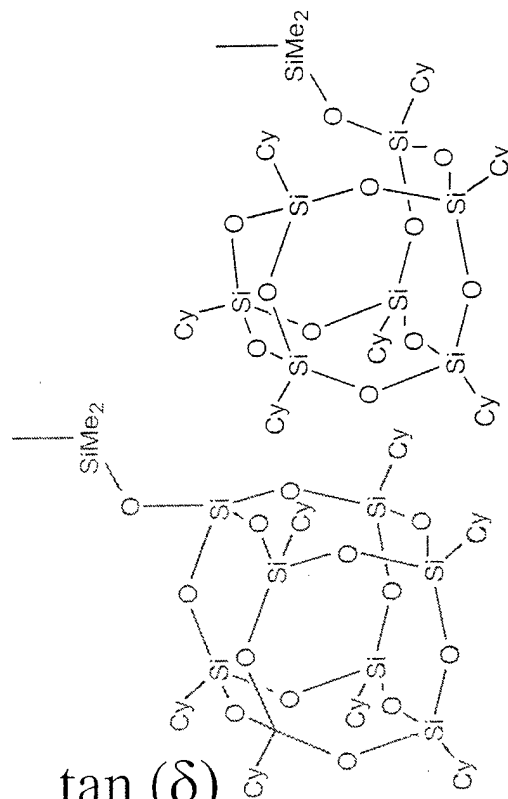


Comparison of Two POSS Polyhedra



PDMS + 5 wt %
CyclohexylPOSS
Red = T8-POSS
Blue = T7-POSS

$\tan(\delta)$

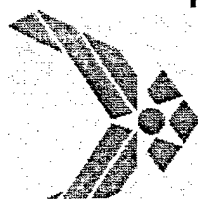


Temperature °C

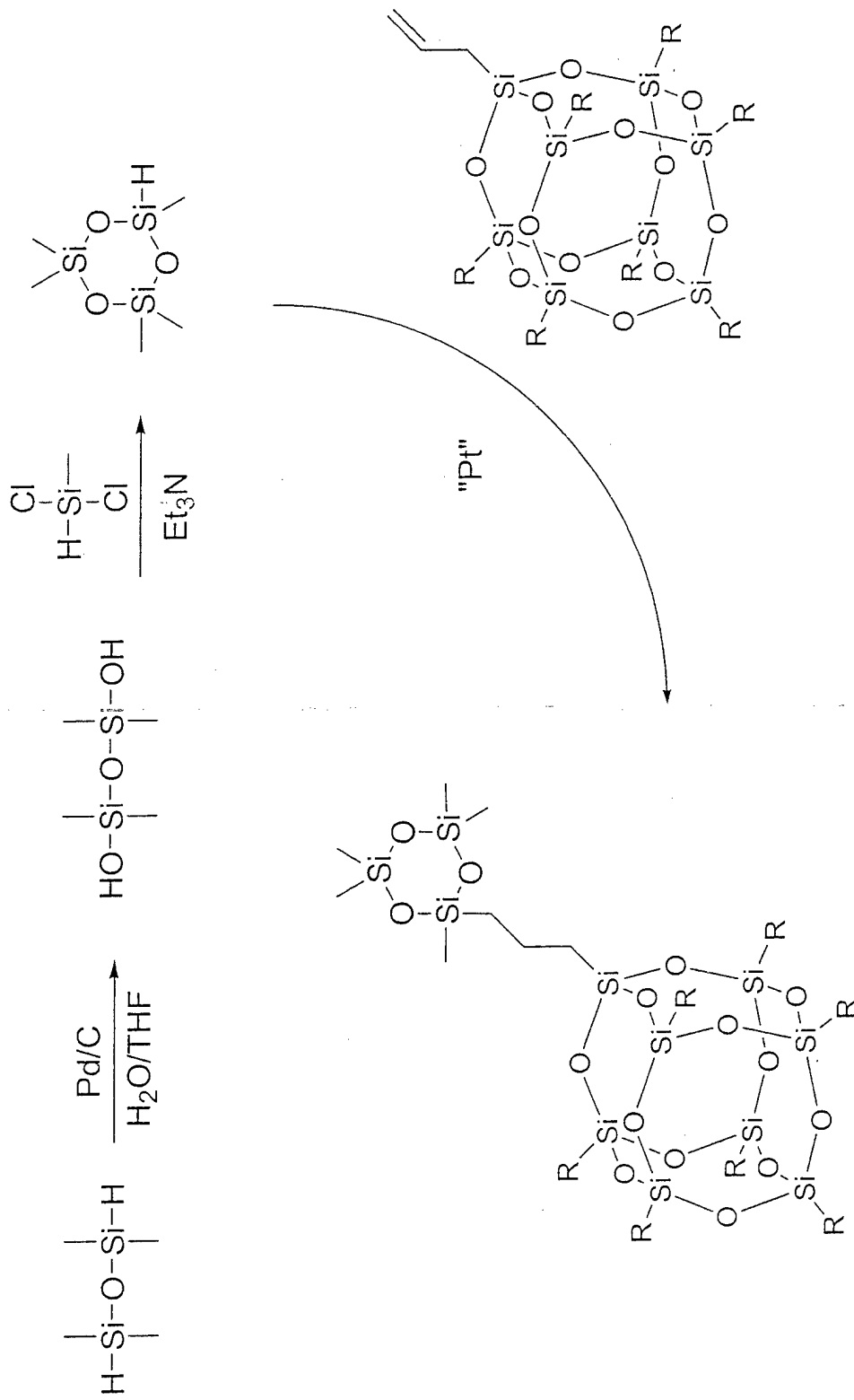
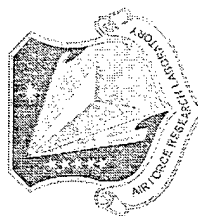
Continue this collaboration with Andre Lee

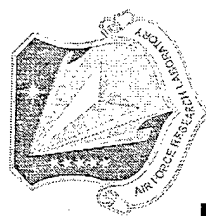
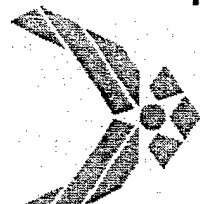
PAS-03-061

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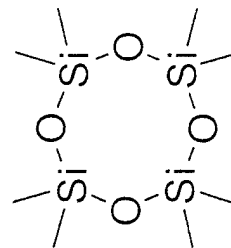
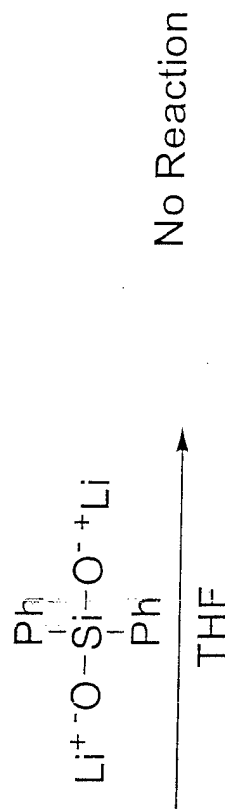
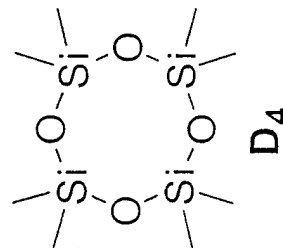
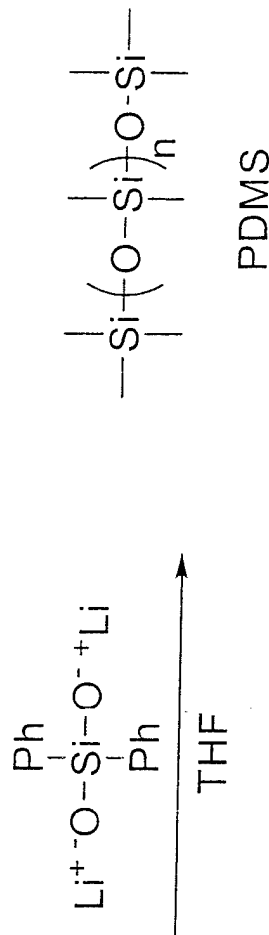
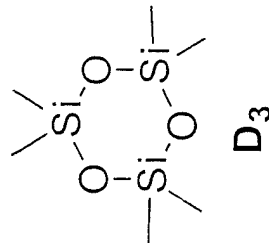


POSS Cyclotrisiloxane

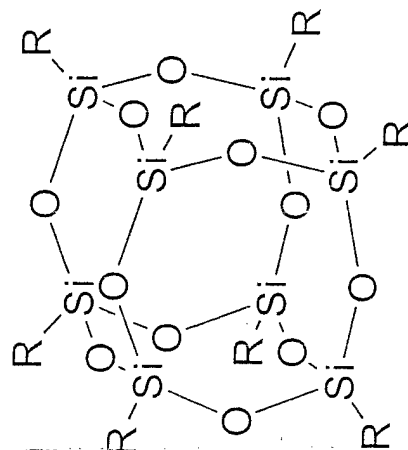




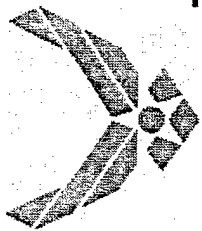
Reactivity



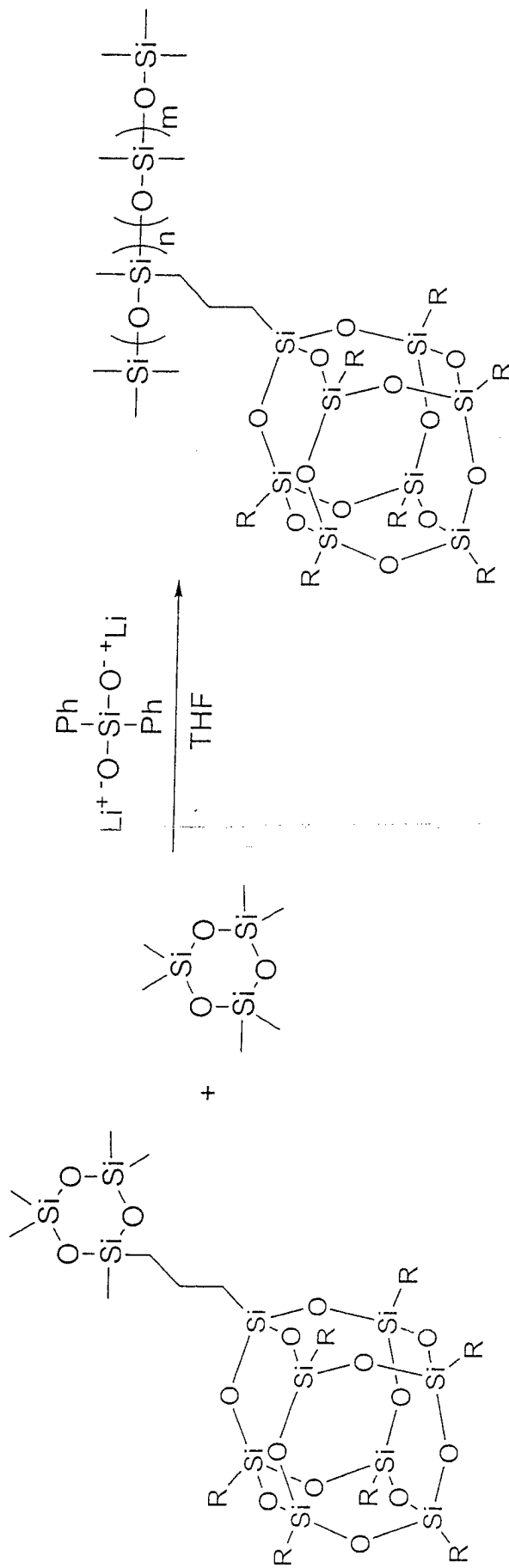
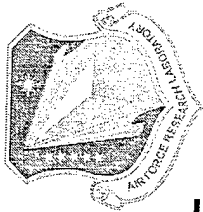
≡

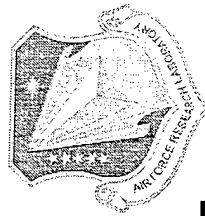
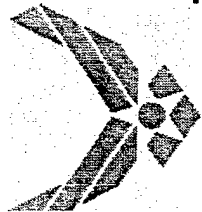


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POSS Siloxane Copolymers

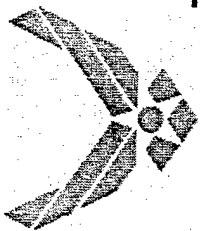




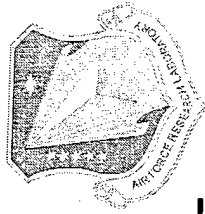
Space-Survivable Materials

PAS-03-061

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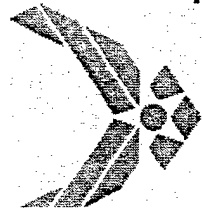


Space Materials

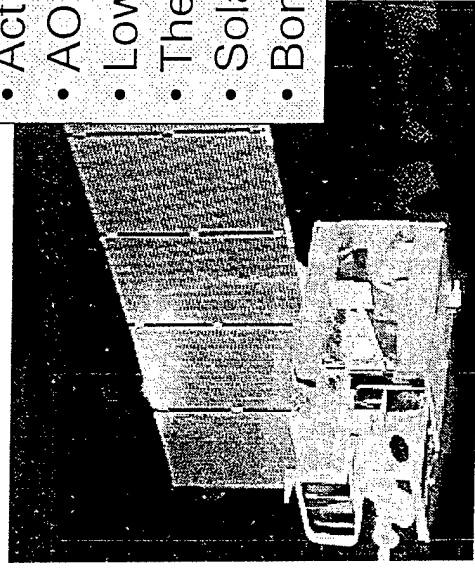
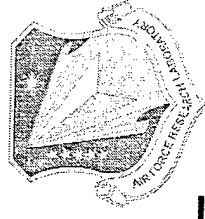


- The International Space Station, the Space Shuttle, and the Hubble Space Telescope are among satellites that operate in Low Earth Orbit (LEO)
- Metallized Teflon FEP is commonly used as outer layer of multi-layer insulation.

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Space-Survivable Polymers



Satellites & Space Systems

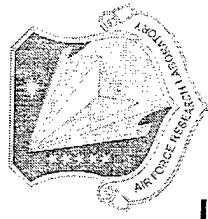
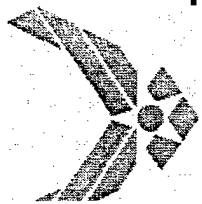
LEO Environment (Altitudes of 200 to 1500 km)

- Atomic Oxygen (AO): $\sim 10^8$ atoms/cm³
- Actual AO flux on spacecraft $\sim 10^{15}$ atoms/cm²•s
- AO Collision energy $\sim 5\text{eV}$ (7.8 km/sec)
- Low-energy and high energy charged particles.
- Thermal cycling -50 to 150°C
- Solar VUV and UV radiation ($\sim 150 - 400$ nm).
- Bond scission and radical formation can lead to embrittlement.

Bond	Dissociation Energy (eV)	λ (nm)	Material
CF ₂ -CF ₂	4.3	290	FEP Teflon®
CF ₂ -F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite

Objectives

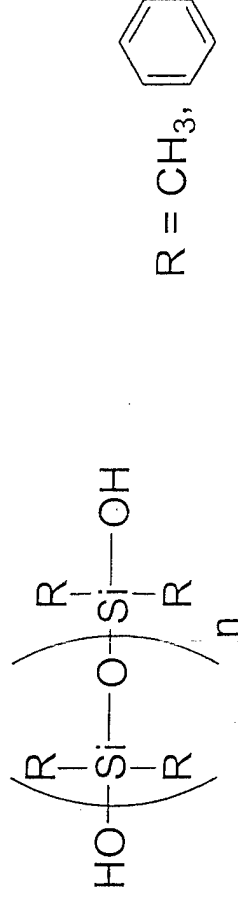
- Increase space-survivability of polymeric materials
- Develop self-passivating layer based on nanocomposite incorporation



Siloxanes

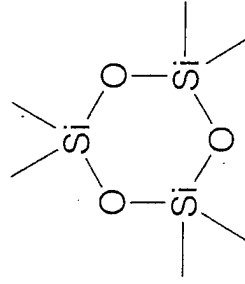
Siloxanes systems exhibit superior resistance to AO

- High Si-O bond strength ~ 8 eV

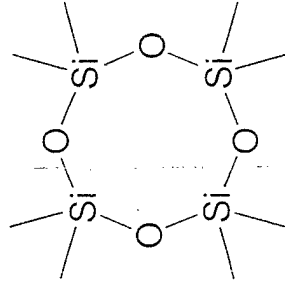


However, pure siloxane systems have disadvantages

- Volatile cyclic species which recondense on optical surfaces



Cyclo(Me₂SiO)₃
(D₃)

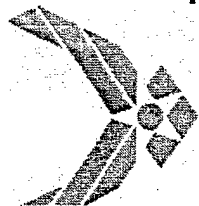


Cyclo(Me₂SiO)₄
(D₄)

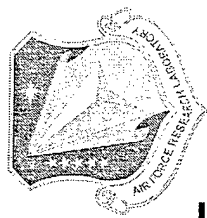
Cyclo(Me₂SiO)₅ (D₅)

Cyclo(Me₂SiO)₆ (D₆)

Cyclo(Me₂SiO)₇ (D₇)



POSS-Siloxane

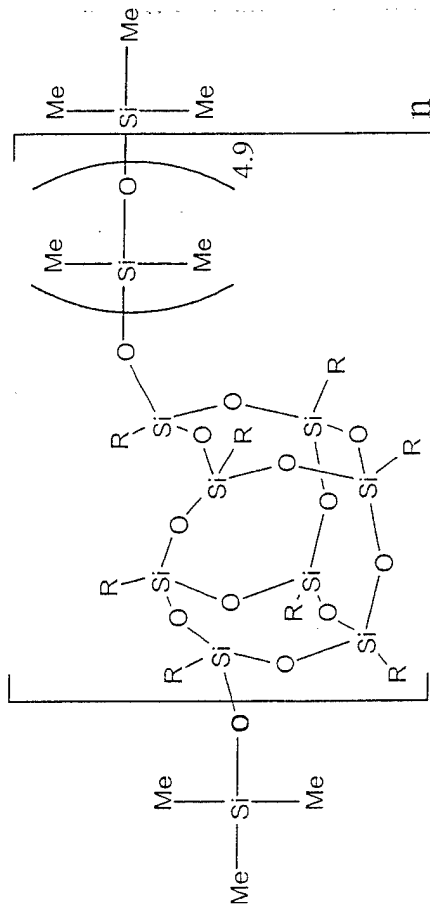


After AO exposure, POSS siloxane had no erosion

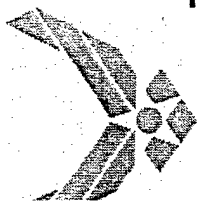
Composition, at %

Sample Treatment	C	O	Si
As entered	65.0	18.5	16.6
2.0 hr	48.4	33.8	17.8
24.6 hr	22.1	49.1	28.8
63.0 hr	16.3	55.7	28.0
4.8 hr air	19.5	52.8	27.7

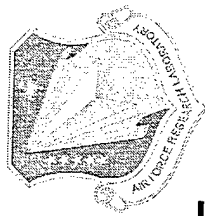
Gonzalez, R. L., Phillips, S. H., Hoflund, G. B., *J. of Spacecraft and Rockets*, Vol 37, No. 4, 2000, pp. 463-467.



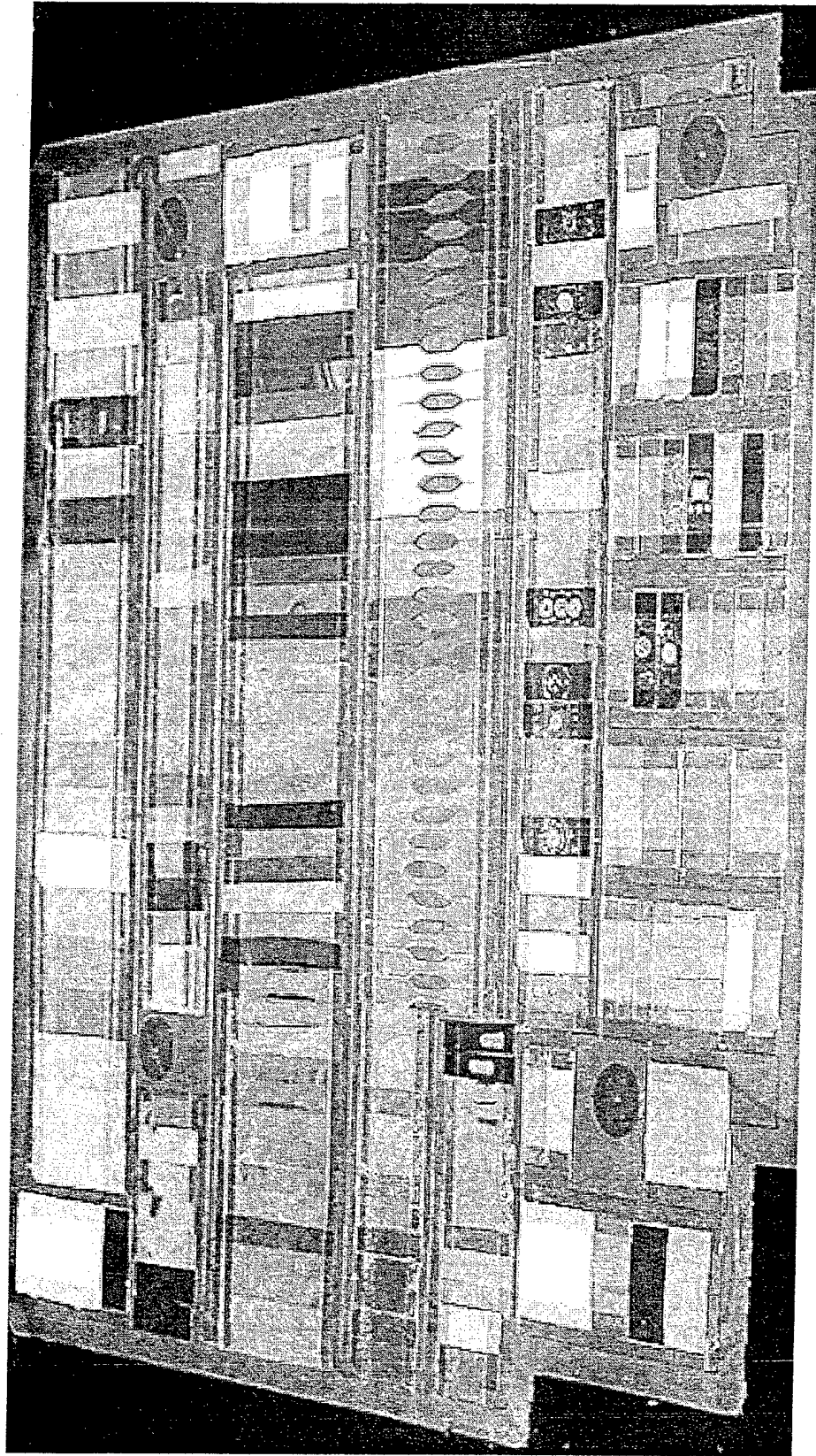
XPS survey spectra obtained from a solvent-cleaned, POSS-PDMS film.



Materials International Space Station Experiment (MISSE)



MISSE 5



Pictures courtesy of NASA

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